ROTATION - ELECTRONIC INTERACTION IN THE 3p -COMPLEX RYDBERG STATE OF WATER

By

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TO MY PARENTS AND TEACHERS
WHO INSPIRED ME TO SEEK
KNOWLEDGE AND WISDOM

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ABSTRACT

An energy theory is formulated for the rotational energy levels in a p-complex Rydberg state of an asymmetric top molecule of symmetry C_{2v}. The effective Hamiltonian used consists of the usual rigid rotor Hamiltonian augmented with terms representing electronic spin and orbital angular momentum effects. Criteria for assigning symmetry species to the rotational energy levels, following Hougan's scheme that uses the full molecular group,are established and given in the form of a table. This is particularly suitable when eigenvectors are calculated on a digital computer. Also, an intensity theory for transitions to the Rydberg p-complex singlet states is presented and selection rules in terms of symmetry species of energy states are established. Finally, applications to H_2O and D_2O are given.

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1. INTRODUCTION

A molecule has a unique structure depending on the atomic masses, electronic distribution, electronic and nuclear spin, inter-particle forces and distances involved. When exposed to an electromagnetic radiation, transitions take place selectively between the energy levels depending upon the frequency of radiation and the selection rules as established by the molecular symmetry and wave function properties. The transitions, characterized by a change in quantum states and identified by the quantum numbers of the interacting energy levels, can be one of the following types.

(1) PURE ROTATIONAL TRANSITIONS

In this case the transitions occur between two different rotational states of energy in the same electronic and vibrational energy levels. The rotational energies are generally more closely spaced than the vibrational levels and, therefore, the corresponding transitions in rotational levels are of relatively low energy and fall in the microwave region.

(2) ROTATION-VIBRATION TRANSITIONS

These transitions occur in the infra-red region and the transitions take place between vibrational levels accompanied by a change in rotational states.

(3) ROVIBRONIC TRANSITIONS

Here, transitions occur from one electronic energy

level to another with a simultaneous change in the vibrational states. Thus the spectrum shows the electronic transitions together with the vibrational and rotational bands. The spectrum lies in the visible and ultraviolet regions.

We are concerned with the rotational energies and dipole transitions to almost degenerate electronic states(say, the p-orbitals) wherein the rotation-electronic matrix elements connecting different rotation-electronic states become significant; the vibrational state, assumed to be the same for all of the almost degenerate electronic states, is not a factor under consideration in our study. The type of molecule considered is an asymmetric top belonging to the C_{2v} point group.

The basic rotational energy theory of asymmetric top molecules has been investigated by many research workers. The theory was first presented by Witmer(1927) and later by Wang (1929) , Klein (1929) and Kramer and Ittmann (1929, 1930). Klein (1929) and later Casimir(1931) have shown that the Wang secular determinant for asymmetric top molecules can be derived by operator techniques thus avoiding the use of an explicit form of a wave function. Ray (1932) introduced asymmetry parameters which by introducing a change of variables greatly facilitated the calculations of energy levels. All the above mentioned theories give the selection rules satisfactorily but none

of these have given a complete classification of the symmetry properties of the wave functions and hence the corresponding energy states. The first effort to this end was made by King, Hainer and Cross (1943, 1949) who have characterized the wave functions according to the Four group $V(x,y,z) = D_2$, defined by an identity and the three two-fold rotation operations C_2^x, C_2^y, C_2^z about the molecule-fixed axes x, y, z respectively. King, Hainer and Cross(1944) have also calculated the line strengths for the electric dipole transitions in a rigid asymmetric rotor where both the initial and the final states are assumed to have the same asymmetry. This theory does not, however, include the electronic-electronic and rotation-electronic interactions that are present in the case in which we are interested. The presence of these interactions in almost degenerate electronic states is expected to affect the rotational energy levels and the corresponding eigenvectors. Consequently, the energy level pattern and intensity distribution are modified accordingly. A proper theory must therefore account for all the interactions involved so as to predict correctly the rotational energies in an electronic state and calculate the relative intensities for the electric dipole transitions.

Creutzberg and Hougen (1967), using Raynes Hamiltonian (1964) as the basis, have discussed the theory of rotational energy levels in near-symmetric rotor molecules of symmetry

C_{2v}, D_2 and D_{2h}. They have considered the effect of spin that results in spin-spin and spin-rotation terms.

The first objective of this thesis is to formulate, for the asymmetric top molecule of symmetry C_{2v}, an energy theory that can take into account explicitly the interactions, arising from both the spin and the orbital angular momenta, present in the nearly degenerate "p-complex" Rydberg state. The "p-complex" Rydberg states, analogous to the atomic situation, are characterized by a well-defined value of orbital angular momentum equal to unity (L=1). The second objective is to formulate an intensity theory, not previously considered, which includes correctly the orbital electronic effects.

We have given in Chapter 2 the well-known rigid rotor theory that includes no interactions. In Chapter 3, the approximate theory for the spin case , given by Creutzberg and Hougen (1967), is adapted for the electronic orbital angular momentum case to obtain the effective rotational constants for $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$ rotation-electronic bands of H_2O as well as D_2O. These rotational constants, in turn, are used in the theory given in Chapter 2 to calculate the rotational energies and the relative intensities so that the results of the theory in Chapter 4, when applied to H_2O and D_2O, may be compared. The numerical details of calculations for H_2O and D_2O for the transitions to the p- complex

Rydberg state, based on our theory in Chapter 4, are given in Chapter 5. Finally, a discussion of the results and conclusions are presented in Chapter 6.

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2. THE RIGID ROTOR THEORY

2.1 RIGID ROTOR HAMILTONIAN

The rotational motion of a molecule in its ground vibronic state may be described, to a good approximation, by a rigid rotor Hamiltonian. We consider, for the sake of generality, an asymmetric top molecule in which case one has the principal moment of inertia $I_x \neq I_y \neq I_z$ and the corresponding rotational constants $X \neq Y \neq Z$ about the principal axes of inertia x, y, z respectively. The classical-mechanical Hamiltonian for a rigid rotor is

$$H = \frac{J_x^2}{2I_x} + \frac{J_y^2}{2I_y} + \frac{J_z^2}{2I_z} \qquad (1)$$

where J_α and I_α ($\alpha = x, y, z$) respectively represent the rotational angular momenta and moments of inertia about the axes α, fixed at the centre-of- mass of the molecule under consideration.

By expressing J_α as operators $\hat{J}_\alpha$ ($\alpha = x, y, z$) and defining the rotational constants $X \neq Y \neq Z$ in cm^{-1} units as

$$X = \frac{\hbar^2}{hc}\cdot\frac{1}{2I_x} \quad ; \quad Y = \frac{\hbar^2}{hc}\cdot\frac{1}{2I_y} \quad ; \quad Z = \frac{\hbar^2}{hc}\cdot\frac{1}{2I_z} \qquad (2)$$

one obtains, on dividing (1) by hc, the quantum-mechanical Hamiltonian for a rigid rotor in cm^{-1} units as

$$\hat{H}_r = \frac{1}{\hbar^2}\left[X\hat{J}_x^2 + Y\hat{J}_y^2 + Z\hat{J}_z^2 \right] \qquad (3)$$

To display diagonal and off-diagonal terms (3) can be rewritten in the form

$$\hat{H}_r = \frac{1}{\hbar^2}\left[\frac{1}{2}(X+Y)\hat{J}^2 + \left\{Z - \frac{1}{2}(X+Y)\right\}\hat{J}_z^2 + \frac{1}{2}(X-Y)(\hat{J}_x^2 - \hat{J}_y^2)\right] \quad (4a)$$

or

$$\hat{H}_r = \frac{1}{\hbar^2}\left[\frac{1}{2}(X+Y)\hat{J}^2 + \left\{Z - \frac{1}{2}(X+Y)\right\}\hat{J}_z^2 + \frac{1}{4}(X-Y)(\hat{J}_+^2 + \hat{J}_-^2)\right] \quad (4b)$$

where

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 \quad (4c)$$

and

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \quad (4d)$$

$\hat{J}_+$ and $\hat{J}_-$ are respectively the lowering and raising operators of angular momentum in the molecule-fixed frame.

The principal moments of inertia I_x, I_y and I_z are usually written as I_a, I_b and I_c where

$$I_a \leq I_b \leq I_c \quad (5a)$$

The corresponding rotational constants X, Y and Z are written as A, B and C where

$$A \geqslant B \geqslant C \quad (5b)$$

For an almost prolate or oblate rotor it is advantageous to choose the molecule-fixed z-axis as the a- or c-axis respectively, since this choice makes the off-diagonal matrix elements small. The prolate description is commonly used for the water molecule since even in this case of a very highly asymmetric top molecule the off-diagonal matrix elements for $z = a$ are smaller than those given by choosing $z = b$ or c. Nevertheless we have, instead, adopted a different scheme. That is, $x = c$, $y = a$, and $z = b$. This choice is consistent with the conventional form of the character table for the C_{2v}

point group as well as chemical convention which requires the $x=c$ axis to be perpendicular to the molecular plane.

Using our choice of axes we now write (4) as

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2 = \hat{J}_c^2 + \hat{J}_a^2 + \hat{J}_b^2 \qquad (5c)$$

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y = \hat{J}_c \pm i\hat{J}_a \qquad (5d)$$

$$\hat{H}_r = \frac{1}{\hbar^2}\left[\frac{1}{2}(C+A)\hat{J}^2 + \left\{B - \frac{1}{2}(C+A)\right\}\hat{J}_b^2 + \frac{1}{4}(C-A)(\hat{J}_+^2 + \hat{J}_-^2)\right] \qquad (5e)$$

Before proceeding to find the rotational energy matrix and, therefore, the rotational energy levels, it seems natural to look for the appropriate functions of states between which matrix elements of $\hat{H}_r$ could be formed. The specific forms of functions, the operators and their effect on rotational functions will be mentioned only briefly in the following section.

2.2 RIGID-ROTOR FUNCTIONS

Since $[\hat{J}_q , \hat{J}_\alpha] = 0$ and $\hat{J}^2$ commutes with space-fixed components $\hat{J}_q$ (q = X,Y,Z-axes in space-fixed coordinates) as well as its molecule-fixed components $\hat{J}_\alpha$, there exist functions $|JKM\rangle$ which are simultaneous eigenfunctions of $\hat{J}^2$, $\hat{J}_z$ and $\hat{J}_Z$ where $\hat{J}_Z$ is the Z-component of $\hat{J}$ in space-fixed coordinate system. The $|JKM\rangle$ are simply the symmetric top eigenfunctions, where

J - rotational quantum number and represents the total rotational angular momentum of the molecule.

K - quantum number representing the component J_z of J and is taken along the symmetry axis of the molecular-fixed frame.

M - quantum number representing the component of total angular momentum along the space-fixed Z-axis.

Note that K and M can each take 2J + 1 values -J, -J + 1, ..., J - 1, J. The quantum numbers J, K and M are shown schematically in the vector model diagram of angular momenta (FIG. 1) where the inter-relationship of J, K and M is quite obvious.

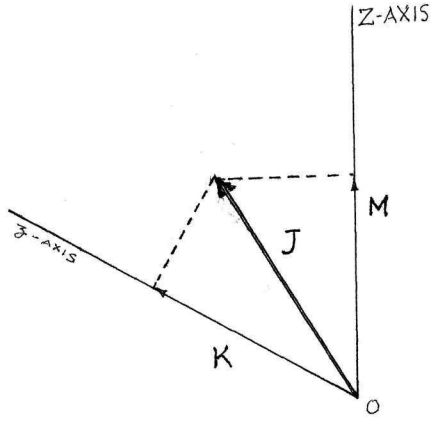

FIG. 1

The functions $|JKM\rangle$ used in this work as basis functions are well known and are given below.

$$|JKM\rangle = C_{JKM}\left(\hat{J}_X - i\hat{J}_Y\right)^{J-M}\left(\hat{J}_c + i\hat{J}_a\right)^{J-K}|JJJ\rangle \quad (6a)$$

where

$$\hat{J}_x \pm i\hat{J}_Y = i\hbar e^{\pm i\varphi}\left(\cot\theta\frac{\partial}{\partial\varphi} \mp i\frac{\partial}{\partial\theta} - \csc\theta\frac{\partial}{\partial\chi}\right) \quad (6b)$$

$$\hat{J}_c \mp i\hat{J}_a = i\hbar e^{\pm i\chi}\left(\csc\theta\frac{\partial}{\partial\varphi} \pm i\frac{\partial}{\partial\theta} - \cot\theta\frac{\partial}{\partial\chi}\right) \quad (6c)$$

$$C_{JKM} = \left(\frac{1}{\hbar}\right)^{2J-K-M}\sqrt{\frac{(J+K)!\,(J+M)!}{[(2J)!]^2\,(J-K)!\,(J-M)!}}$$

and

$$|JJJ\rangle = \sqrt{\frac{2J+1}{8\pi^2}}\, e^{iJ(\varphi+\chi)} \left(\cos\frac{\theta}{2}\right)^{2J} \tag{6d}$$

where θ, φ, χ are the Euler angles which relate the space-fixed coordinates to the molecule-fixed coordinates.

In a homogeneous space the energy is independent of M; therefore we can drop this quantum number in our future notations. That is, $|JKM\rangle$ will be represented by $|JK\rangle$ from now on. Thus $|JK\rangle$ will be taken as a basis functions to yield the asymmetric-top rotational energy stationary states and eigenfunctions on diagonalization of $\hat{H}_r$. The effect of operators $\hat{J}_\pm = \hat{J}_c \pm i\hat{J}_a$, $\hat{J}_z \equiv \hat{J}_b$ and $\hat{J}^2$ on the functions are

$$\hat{J}_\pm |JK\rangle = (\hat{J}_c \pm i\hat{J}_a)|JK\rangle = \sqrt{J(J+1) - K(K\mp 1)}\,\hbar\,|JK\mp 1\rangle \tag{7}$$

$$\hat{J}_b |JK\rangle = K\hbar\,|JK\rangle \tag{8}$$

$$\hat{J}^2 |JK\rangle = J(J+1)\hbar^2 |JK\rangle \tag{9}$$

which will be used to yield diagonal and off-diagonal matrix elements of the rigid rotor Hamiltonian. Note that (7) results from the "anomalous" sign of "i" (see [21]).

2.3 RIGID ROTOR MATRIX ELEMENTS

Operating the rigid rotor Hamiltonian $\hat{H}_r$ on $|JK\rangle$ on the right hand side in (5a) and using the results (7), (8) and (9) gives

$$\begin{aligned}\hat{H}_r |JK\rangle &= \frac{1}{\hbar^2}\left[\tfrac{1}{2}(C+A)\hat{J}^2 + \left\{B - \tfrac{1}{2}(C+A)\right\}\hat{J}_b^2 + \tfrac{1}{4}(C-A)(\hat{J}_+^2 + \hat{J}_-^2)\right]|JK-2\rangle \\ &= \left[\tfrac{1}{2}(C+A)[J(J+1)] + [B - \tfrac{1}{2}(C+A)]K^2\right]|JK\rangle \\ &\quad + \left[\tfrac{1}{4}(C-A)\sqrt{[J(J+1) - K(K-1)][J(J+1) - (K-1)(K-2)]}\right]|JK-2\rangle \\ &\quad + \left[\tfrac{1}{4}(C-A)\sqrt{[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)]}\right]|JK+2\rangle\end{aligned}$$

which on multiplying with $\langle JK|$, $\langle JK-2|$ and $\langle JK+2|$ gives the matrix elements

$$\langle JK|\hat{H}_r|JK\rangle = \tfrac{1}{2}(C+A)[J(J+1)] + [B - \tfrac{1}{2}(C+A)]K^2 \qquad (10a)$$

and

$$\langle JK\pm 2|\hat{H}_r|JK\rangle = \tfrac{1}{4}(C-A)\sqrt{[J(J+1) - K(K\pm 1)][J(J+1) - (K\pm 1)(K\pm 2)} \qquad (10b)$$

where the orthonormality condition

$$\langle JK'|JK\rangle = \delta_{KK'} = \begin{cases} 1 & \text{if } K' = K \\ 0 & \text{if } K' \neq K \end{cases} \qquad (10c)$$

is used for the basis functions to obtain (10a) and (10b). Although (10a) and (10b) can be used directly to calculate the rotational energy levels, we have used an asymmetry parameter κ [19] because it facilitates the

calculation of the rotational stationary states by using scaled rotational constants, thereby making it possible to carry out solutions, at least in part, for all molecules. On replacing A,B and C respectively with

$$\sigma A + \rho \quad ; \quad \sigma B + \rho \quad ; \quad \sigma C + \rho \tag{11}$$

in the rotational Hamiltonian

$$\hat{H}_r\,(A,B,C) = \frac{1}{\hbar^2}\left[A\hat{J}_a^{\,2} + B\hat{J}_b^{\,2} + C\hat{J}_c^{\,2}\right] \tag{12}$$

one obtains

$$\begin{aligned}\hat{H}_r\,(\sigma A+\rho, \sigma B+\rho, \sigma C+\rho) &= \frac{1}{\hbar^2}\left[(\sigma A+\rho)\hat{J}_a^{\,2} + (\sigma B+\rho)\hat{J}_b^{\,2} + (\sigma C+\rho)\hat{J}_c^{\,2}\right] \\ &= \sigma\hat{H}_r\,(A,B,C) + \frac{\rho}{\hbar^2}\hat{J}^2\end{aligned} \tag{13}$$

where $\hat{J}^2 = \hat{J}_a^{\,2} + \hat{J}_b^{\,2} + \hat{J}_c^{\,2}$.

The resulting matrix elements are then

$$\langle JK'|\,\hat{H}_r\,(\sigma A+\rho, \sigma B+\rho, \sigma C+\rho)\,|JK\rangle = \sigma\langle JK'|\,\hat{H}_r\,(A,B,C)\,|JK\rangle + \rho J(J+1)\delta_{KK'} \tag{14}$$

Following Ray [19] , we set

$$\sigma A + \rho = 1 \quad ; \quad \sigma B + \rho = K \quad ; \quad \sigma C + \rho = -1 \tag{15a}$$

which give

$$\sigma = \frac{2}{A-C} \quad ; \quad \rho = -\frac{A+C}{A-C} \quad ; \quad K = \frac{2B-(A+C)}{A-C} \tag{15b}$$

Use of (15a) and (15b) in (14) gives

$$\langle JK' | \hat{H}_r(1, \kappa, -1) | JK \rangle = \frac{2}{A-C} \langle JK' | \hat{H}_r(A, B, C) | JK \rangle - \frac{A+C}{A-C} J(J+1)\delta_{KK'} \tag{16}$$

or

$$\langle JK' | \hat{H}_r(A, B, C) | JK \rangle = \frac{A-C}{2} \langle JK' | \hat{H}_r(1, \kappa, -1) | JK \rangle + \frac{A+C}{2} J(J+1)\delta_{KK'} \tag{17}$$

The scaled matrix $\langle JK | \hat{H}_r(1, \kappa, -1) | JK \rangle$, which depends on the asymmetry parameter κ, when diagonalized gives the energy levels

$$E(A, B, C) = \frac{A+C}{2} J(J+1) + \frac{A-C}{2} E(\kappa) \tag{18}$$

where

$$E(\kappa) = \langle JK | \hat{H}_r(1, \kappa, -1) | JK \rangle \tag{19}$$

The parameter κ, which measures the degree of asymmetry, ranges between 1 and -1; i.e., between $\sigma A + \rho$ and $\sigma C + \rho$, κ being -1 for the prolate symmetric top limit while it is 1 for the oblate symmetric top limit and $\kappa = 0$ for the most asymmetric top limit case.

2.4 LABELLING THE ENERGY LEVELS:

For an asymmetric top rotor, both J, the total angular momentum and its projection M along the space-fixed Z-axis are constants of motion, and, therefore, are good quantum numbers. They can be used to specify the energy states of a rotor. The component of angular

momentum in any direction in the molecule-fixed frame is, however, not constant; be it a classical mechanical motion or a quantum-mechanical one. Thus, $[\hat{H}_r, \hat{J}_z] \equiv [\hat{H}_r, \hat{J}_b] \neq 0$ and K is not a good quantum number. K cannot be used adequately to specify the rotational energy states. Thus far, no set of quantum numbers is known for the asymmetric top molecules which conveniently specify the stationary states of the rotor and have a simple physical meaning. Regardless of the inadequacy of K to be a good quantum number, it is retained to label the energy levels in the form $J_{K_{-1}K_1}$ (or $J_{K_a K_c}$) where K_{-1}(or K_a) and K_1(or K_c) are the values K will acquire in the limiting cases of prolate symmetric top and oblate symmetric top. The subscripts -1 and 1 appearing with K are the parametric values of K under the extreme limits. There is an equivalent scheme of labelling the energy states, represented by J_τ where $\tau = K_{-1} - K_1 = K_a - K_c$. Assuming the states for a given J value are listed in order of increasing energy the labels $K_a = 0,1,1,2,2,\ldots,J,J$, $K_c = J,J,J-1,J-1,\ldots,1,1,0$ and thus $\tau = -J, -J+1, \ldots, J-1, J$ are attached to each state, starting from that of lowest energy for a particular J value.

In our work, the latter scheme is adopted; that is, the J_τ symbol is used for labelling the energy states. The labelling scheme is shown in FIG. 2.

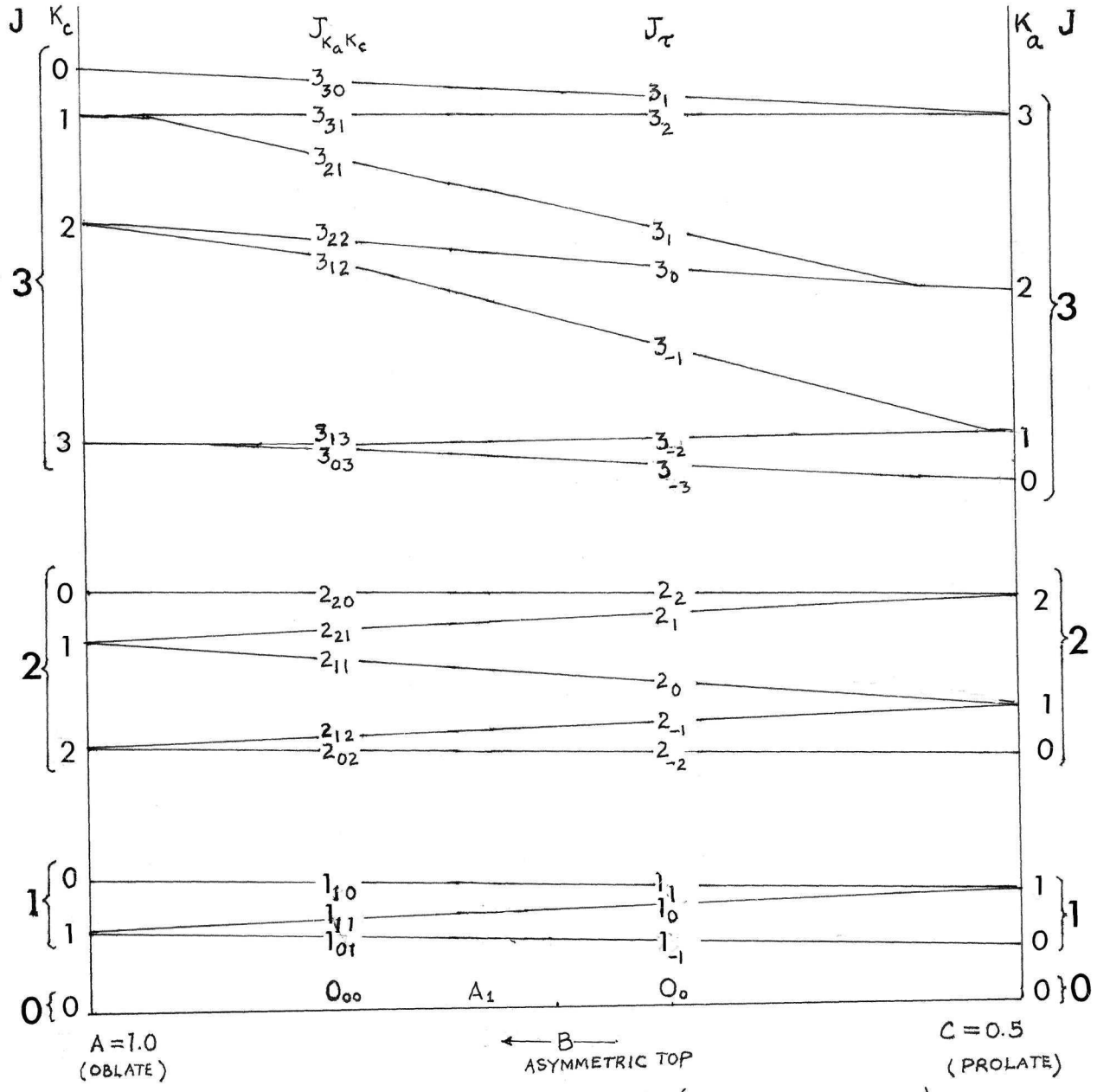

FIG 2. THE TWO LABELLING SCHEMES ($J_{K_a K_c}$ AND J_τ).

2.5 TRANSFORMATION PROPERTIES OF RIGID ROTOR BASIS FUNCTIONS:

The transformation properties of rigid rotor basis functions are important from the view point of classification of symmetry of energy levels and determining the combination of states involved in transitions.

Hougen (1963) has given the following effect of symmetry transformations.

$$\hat{C}_{2z}|JK\rangle \equiv \hat{C}_{2b}|JK\rangle = (-1)^K|JK\rangle \qquad (20a)$$

$$\hat{\sigma}_v(yz)|JK\rangle \equiv \hat{\sigma}_v(ab)|JK\rangle = (-1)^J|J-K\rangle \qquad (20b)$$

$$\hat{\sigma}_v(xz)|JK\rangle \equiv \hat{\sigma}_v(cb)|JK\rangle = (-1)^{J-K}|J-K\rangle \qquad (20c)$$

These results will be used in our work.

2.6 CLASSIFICATION SCHEMES FOR ENERGY STATES:

There are two schemes which can be used to classify the energy levels, based on either

(i) molecular subgroup and parity

or (ii) full molecular point group.

For planar molecules, Hougen [9] has shown that reflection in the molecular plane is equivalent to the parity operation. Then the molecular plane $\sigma_v(yz)$ when used as an operator on the complete wavefunction, determines the parity of states. Therefore, the scheme (ii), based on the full molecular symmetry group,

embodies within its framework the ability of assigning parity to energy levels. The scheme, first introduced by Hougen [8], will be used in the present work to replace the earlier scheme of representing the energy levels by ++, +-, -+, -- and also + , - for designating the parity of purely rotational states.

Hougen's scheme has the advantage of using the actual molecular point group rather than simply the D_2 group of a rigid rotor. In the earlier scheme (i), one also needs to label the energy states by a (asymmetric) or s (symmetric) according as the permutation of nuclei changes sign of the complete wavefunction (excluding nuclear spin) or not. This is done by examining the rotational subgroup. Thus, in Hougen's scheme the full molecular group labels belonging to the same rotational subgroup species have the same statistical weight.

2.7 THE ASYMMETRIC TOP RIGID ROTOR EIGENFUNCTIONS AND ASSIGNMENT OF SYMMETRY SPECIES

Let the rigid rotor wavefunction corresponding to the energy level, denoted by τ, in the basis $|JK\rangle$ be given by

$$\psi_r^{\tau} = \sum_K a_K^{\tau} |JK\rangle \qquad (21)$$

where ψ_r^{τ} is expressed as a linear combination of eigenvectors a_K^{τ} of energy level (labelled as τ) taken

over all possible values of quantum number K in the basis $|JK\rangle$.

In order to determine the symmetry of an energy state we use the elements of the molecular point group as operators on the rotational eigenfunctions in conformity with the transformation properties (20a) and (20b). Then we look for the behaviour of the eigenfunctions with reference to the associated irreducible representations or characters as decided by the even-odd nature of the quantum numbers J and K. Thus, from (20a), (20b), (21) and the character table for the C_{2v} point group (APPENDIX I), we find that

$$\hat{C}_{2z}\psi_r^\tau \equiv \hat{C}_{2z}\sum_K a_K^\tau |JK\rangle = \sum_K (-1)^K a_K^\tau |JK\rangle \quad (22)$$

Since $\psi_r^\tau = \pm \psi_r^\tau$, (22) implies that

$$\hat{C}_{2z}\psi_r^\tau = \begin{cases} +\psi_r^\tau & \text{for even} \quad K\text{-values} \\ -\psi_r^\tau & \text{for odd} \quad K\text{-values} \end{cases} \quad (23a)$$

Then the character table indicates that

K-EVEN is associated with species A_1 or A_2 and
K-ODD is associated with species B_1 or B_2 (23b)

Also

$$\hat{\sigma}_v(yz)\psi_r^\tau = \hat{\sigma}_v(yz)\sum_K a_K^\tau |JK\rangle = (-1)^J \sum_K a_K^\tau |J-K\rangle \quad (24a)$$

There are two possibilities; either (24a) is equal to $+\psi_r^\tau$ or $-\psi_r^\tau$.

Let us now suppose that

$$a_K^\tau = a_{-K}^\tau \tag{24b}$$

then (24a) becomes

$$\hat{\sigma}_v(yz)\psi_r^\tau = (-1)^J \sum_K a_{-K}^\tau |J-K\rangle = (-1)^J \psi_r^\tau \tag{24c}$$

since K is merely a summation index.

Similarly, if

$$a_K^\tau = -a_{-K}^\tau \tag{24d}$$

then

$$\hat{\sigma}_v(yz)\psi_r^\tau = -(-1)^J \psi_r^\tau \tag{24e}$$

The results (24a), (24b), (24c), (24d) and (24e) lead to the conclusion that

$$\hat{\sigma}_v(yz)\psi_r^\tau = \pm (-1)^J \psi_r^\tau \quad \text{if} \quad a_K^\tau = \pm a_{-K}^\tau \tag{24f}$$

Again from (24f) and the character table for C_{2v} point group, we find that

$$\hat{\sigma}_v(yz)\psi_r^\tau = \begin{cases} +\psi_r^\tau & \text{refers to species } A_1 \text{ or } B_2 \\ -\psi_r^\tau & \text{refers to species } A_2 \text{ or } B_1 \end{cases} \tag{24g}$$

We do not use $\hat{\sigma}_v(xz)$ since it leads to no additional information not already contained in (23b) and (24g).

The results (23a), (23b) and (24f), (24g) lead us to

establish the following criteria (TABLE 1) for the assignment of symmetry species to the rotational energy states.

TABLE 1

CRITERIA FOR ASSIGNING THE FULL MOLECULAR SPECIES TO THE RIGID ROTOR ENERGY STATES OF THE MOLECULES OF SYMMETRY C_{2v}

J	K	$a_K^\tau = a_{-K}^\tau$		$a_K^\tau = -a_{-K}^\tau$	
		SYMMETRY SPECIES	PARITY	SYMMETRY SPECIES	PARITY
EVEN	EVEN	A_1	+	A_2	-
EVEN	ODD	B_2	+	B_1	-
ODD	EVEN	A_2	-	A_1	+
ODD	ODD	B_1	-	B_2	+

Note that the parity results are obtained from $\hat{\sigma}_v(yz)$ alone. That is, A_1 and B_2 levels are of + (i.e. even) parity while A_2 and B_1 levels are of - (i.e. odd) parity.

2.8 DIPOLE TRANSITION MOMENTS

Electric dipole transitions are governed by the square of the integral

$$\langle \psi'_{evr} \mid \mu_Z \mid \psi''_{evr} \rangle \tag{25}$$

where μ_Z is the space-fixed Z-component of the electric dipole moment $\vec{\mu}$ while ψ''_{evr} and ψ'_{evr} are the rovibronic eigenfunctions corresponding to the initial and final states, respectively, involved in the transition.

Under the group operations, any space-fixed polar vector changes sign under improper rotations and is invariant under proper rotations. Then, using the C_{2v} character table, we see that the irreducible representation for μ_Z, denoted by $\Gamma(\mu_Z)$, is of species

$$\Gamma(\mu_Z) = A_2 \tag{26}$$

The integral (25) must be totally symmetric in order to exist. This requires, in view of (26), ψ''_{evr} and ψ'_{evr} to be of opposite parity. In other words, the direct product of their symmetry species must obey

$$\Gamma(\psi'_{evr}) \times \Gamma(\psi''_{evr}) = A_2 \tag{27}$$

In practice, it is convenient to classify the rovibronic states for a totally symmetric vibronic state. The complete symmetry species for any rovibronic state is then obtained simply by multiplying the rotational species with the vibronic species. This requires

different selection rules for different vibronic transactions, obtained from (27) as follows:

Use of the Born-Oppenheimer opproximation allows us to write the full (rovibronic) eigenfunction ψ_{evr} as a product of vibronic and rotational wavefunctions ψ_{ev} and ψ_r respectively. That is,

$$\psi_{evr} = \psi_{ev}\,\psi_r \tag{28}$$

Then one can write

$$\Gamma(\psi_{evr}) = \Gamma(\psi_{ev}) \times \Gamma(\psi_r) \tag{29}$$

which when used in (27) yields

$$\left[\Gamma(\psi_r') \times \Gamma(\psi_r'')\right] \times \left[\Gamma(\psi_{ev}') \times \Gamma(\psi_{ev}'')\right] = A_2 \tag{30}$$

giving the rule

$$\Gamma(\psi_r') \times \Gamma(\psi_r'') = \Gamma(\psi_{ev}') \times \Gamma(\psi_{ev}'') \times A_2 \tag{31}$$

which sets the criterion for determining the possible transitions between rotational states for fixed symmetry species of vibronic states in the initial and final states of transitions. The possible cases for which transitions might occur between rotation-electronic states will be considered one by one at a later stage after general forms of expressions for the line strength and relative intensity have been developed.

2.9 TRANSITION MOMENTS IN THE MOLECULAR-FIXED FRAME

Since the components of the dipole moment must be used in the molecule -fixed frame for a rotating molecule, it is important to know the form of transformation of the space-fixed component μ_Z to the molecule -fixed frame.

Let $$f_{Z\alpha} = f_{Z\alpha}(\theta, \varphi, \chi) \text{ where } \alpha = x, y, z \quad (32)$$

be the functions of Euler angles θ, φ and χ ([8], [13]) which are associated with the molecule -fixed components μ_α of μ_Z according to the equation

$$\mu_Z = \sum_{\alpha = x, y, z} f_{Z\alpha}(\theta, \varphi, \chi)\mu_\alpha \quad (33)$$

We consider μ_α in the form

$$\mu_0 \equiv \mu_z \quad \text{and} \quad \mu_\pm = (\mu_x \pm i\mu_y)/\sqrt{2} \quad (34)$$

so (33) takes the form

$$\mu_Z = \sum_r f_{-r}\mu_r \quad ; \quad r = 0, \pm 1 \quad (35)$$

where f_{-r} are appropriate functions of the direction cosines and μ_r are the components ofa spherical tensor of rank unity. Therefore, the form of the electric dipole transition moments (25) changesto

$$\langle \psi'_{evr} | \sum_r f_{-r}\mu_r | \psi''_{evr} \rangle \quad (36)$$

which will be used in our future development of intensity relations.

2.10 EXPRESSIONS FOR LINE STRENGTHS AND RELATIVE INTENSITIES:

The line strength $[S]^{J''}_{J'}$ which gives the probability of transition between the states involved is given by the spatial average (see Lepard [13]),

$$[S]^{J''}_{J'} = \overline{|\langle \psi'(J') | \mu_z | \psi''(J'') \rangle|^2} = \tfrac{1}{3}[G]^{J''}_{J'} \tag{37}$$

where

$$[G]^{J''}_{J'} = \left| \sum_{K'',K'} a^{\tau''}_{K''} a^{\tau'}_{K'} \langle e'v'; J'K' | \sum_r f_{-r} \mu_r | e''v''; J''K'' \rangle \right|^2 \tag{38}$$

In (38), $|ev\,;\,JK\rangle$ are the basis functions of the rovibronic eigenfunctions ψ_{evr} and, in view of the approximation (28), can be written in the form.

$$|ev\,;\,JK\rangle = |ev\rangle|JK\rangle \tag{39}$$

Also f_{-r} are now the reduced operators which no longer depend on the magnetic quantum number M . Then (38) may be rewritten as

$$[G]^{J''}_{J'} = \left| \sum_{K'',K',r} a^{\tau''}_{K''} a^{\tau'}_{K'} \langle e'v' | \mu_r | e''v'' \rangle \langle J'K' | f_{-r} | J''K'' \rangle \right|^2 \tag{40}$$

Then, assuming that the absorption layer is thin, the expression for the line strength becomes

$$[S]^{J''}_{J'} = \frac{1}{3} \left| \sum_{K'',K',r} a^{\tau''}_{K''} a^{\tau'}_{K'} \langle e'v' | \mu_r | e''v'' \rangle \langle J'K' | f_{-r} | J''K'' \rangle \right|^2 \tag{41}$$

Note that $r = \Delta K = K' - K'' = 0, \pm 1$ and $\Delta J = J' - J'' = 0, \pm 1$ (See Lepard [13]).

Then the expression for the relative intensities of transitions may be written as

$$[I]_{J'}^{J''} = \nu g_{J''} (2J''+1) e^{-E/T^*} \cdot \frac{1}{3} \left| \sum_{K'',K',r} a_{K''}^{\tau''} a_{K'}^{\tau'} \langle e'v' | \mu_r | e''v'' \rangle \langle J'K' | f_{-r} | J''K'' \rangle \right|^2 \qquad (42)$$

where

ν = Frequency of absorption

$g_{J''}$ = Nuclear statistical weight for the initial state corresponding to the rotational quantum number

E = Energy of the lower state in cm^{-1}

$T^* = T/\left(\frac{hc}{k}\right)$ = T /(SECOND RADIATION CONSTANT) in which

T = Temperature in absolute units (^oK)

and k = Boltzmann constant.

The non-vanishing matrix elements given by Johns and Lepard [12] are listed here in TABLE 2. (Note that K is used here in place of Ω).

TABLE 2

MATRIX ELEMENTS $\langle J'K' | f_{-r} | J''K'' \rangle$

	K'	
J'	K''	$K''\pm 1$
J''	$\dfrac{K''}{\sqrt{J''(J''+1)}}$	$\sqrt{\dfrac{(J''\mp K'')(J''\pm K''+1)}{2J''(J''+1)}}$
$J''+1$	$\sqrt{\dfrac{[(J''+1)^2-K''^2]}{(J''+1)(2J''+1)}}$	$\mp\sqrt{\dfrac{(J''\pm K''+1)(J''\pm K''+2)}{2(J''+1)(2J''+1)}}$
$J''-1$	$\sqrt{\dfrac{[J''^2-K''^2]}{J''(2J''+1)}}$	$\pm\sqrt{\dfrac{(J''\mp K'')(J''\mp K''-1)}{2J''(2J''+1)}}$

Now we proceed to consider the possible cases of transitions that may occur between the rotation-electronic states in conformity with the criterion given in (31). Based on the combination of states and the real and imaginary nature of vibronic integrals as decided by the time reversal operator and symmetry elements of the point group, it is possible to obtain the relations for the line strengths and relative intensities for each possible case using (41) and (42).

CASE (1) $\Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = A_1$

Since the product of the vibronic states ψ'_{ev} and ψ''_{ev} is of symmetry species A_1, we observe from (31) that one must have

$$\Gamma(\psi_r') \times \Gamma(\psi_r'') = A_2 \qquad (43a)$$

Then, from group theory, the only possible transitions are

$$A_1 \longleftrightarrow A_2 \qquad \text{and} \qquad B_1 \longleftrightarrow B_2$$

where the species are the full molecular group species for the rotational functions. Such transitions also depend on the existence of vibronic integrals

$$\langle \psi'_{ev} \mid \mu_\alpha \mid \psi''_{ev} \rangle \tag{43b}$$

where $\mu_\alpha (\alpha = x, y, z)$ are the molecule-fixed components of the dipole moment. It requires, in the present case, that

$$\Gamma(\mu_\alpha) = \Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = A_1 \tag{43c}$$

Thus the transitions are governed by μ_z alone. We, therefore, conclude that the following transitions are allowed between the rotational states

$$\left.\begin{array}{ll} & A_1 \longleftrightarrow A_2 \qquad \text{and} \qquad B_1 \longleftrightarrow B_2 \\ \text{FOR} & \Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = A_1 \quad \text{and} \quad \Gamma(\mu_z) = A_1 \end{array}\right\} \tag{43d}$$

It is important to know whether the vibronic integral is real or imaginary, because this information simplifies the line strength and relative intensity calculations. This is done by looking at the effect of the time-reversal operator $\hat{\theta}_t$, which simply performs complex conjugation, on the vibronic integral.

The vibronic integral is real or imaginary according as the integral remains invariant or changes sign because of the effect of $\hat{\theta}_t$. In some cases, additional information is required regarding the effect of symmetry group elements on the vibronic integral.

In view of the fact that

$$\hat{\theta}_t \mu_z \equiv \hat{\theta}_t \mu_o = \mu_o \tag{44a}$$

and

$$\hat{\theta}_t \mu_\pm = \mu_\mp \tag{44b}$$

and if we assume, for the sake of convenience, that the functions ψ'_{ev} and ψ''_{ev} and hence their corresponding basis functions $|e'v'\rangle$ and $|e''v''\rangle$ are real, then

$$\hat{\theta}_t \langle e'v' | \mu_o | e''v'' \rangle = \langle e'v' | \mu_o | e''v'' \rangle$$

That is,

$$\hat{\theta}_t \langle \mu_o \rangle = \langle \mu_o \rangle \equiv \langle \mu_z \rangle \tag{44c}$$

(44c) shows that $\langle \mu_z \rangle$ is invariant under the time-reversal operation, and, therefore, it is real.
Then from (44c) and (41), one obtains the line strengths

$$[S]^{J''}_{J'} = \frac{1}{3} \left| \sum_{K''} a^{\tau''}_{K''} a^{\tau'}_{K''} \langle e'v' | \mu_o | e''v'' \rangle \langle J'K'' | f_o | J''K'' \rangle \right|^2$$

or

$$[S]^{J''}_{J'} = \frac{\langle \mu_z \rangle^2}{3} \left| \sum_{K''} a^{\tau''}_{K''} a^{\tau'}_{K''} \langle J'K'' | f_o | J''K'' \rangle \right|^2 \tag{45a}$$

and,using (42), the corresponding relative intensities are

$$[I]^{J''}_{J'} = \nu g_{J''}(2J''+1)e^{-E/T^*}\frac{\langle \mu_z \rangle^2}{3}\left|\sum_{K''} a^{\tau''}_{K''}\, a^{\tau'}_{K''}\langle J'K''|f_0|J''K''\rangle\right|^2 \tag{45b}$$

Here a well established fact that $\Delta K = 0$ for μ_z is used. The values of $\langle J'K''|f_0|J''K''\rangle$ can be seen in TABLE 2.

CASE (2): $\Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = A_2$

From (31), we must have in this case

$$\Gamma(\psi'_r) \times \Gamma(\psi''_r) = A_1 \tag{46a}$$

which is possible only if

$$\Gamma(\psi'_r) = \Gamma(\psi''_r) = \text{SAME SPECIES} \tag{46b}$$

However, the requirement

$$\Gamma(\mu_\alpha) = A_2 \tag{46c}$$

shows that CASE (2) is not allowed since μ_x, μ_y and μ_z belong to the species B_1, B_2 and A_1 respectively. Therefore, transitions between the rotational states having the same symmetry species are forbidden. This conclusion is consistent with the fact that transitions can occur only between the energy states of opposite parity and not between those of the same parity. Thus the line strengths and, consequently, the relative intensities will be zero whenever the CASE (2) is encountered.

CASE (3): $\Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = B_1$

Similar to the procedure adopted in CASES (1) and (2), we find from (31) that

$$\Gamma(\psi_r') \times \Gamma(\psi_r'') = B_2 \tag{47a}$$

Then (47a) and the use of group theory leads to the possible transitions between the rotational states

$$A_1 \leftrightarrow B_2 \quad \text{and} \quad A_2 \leftrightarrow B_1$$

Also

$$\Gamma(\mu_\alpha) = \Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = B_1 \tag{47b}$$

in this case. We see from (47b) that transitions are governed by μ_x. Hence the allowed transitions between the rotational states are

$$\left.\begin{aligned} &A_1 \leftrightarrow B_2 \quad \text{and} \quad A_2 \leftrightarrow B_1 \\ &\text{for } \Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = B_1 \text{ and } \Gamma(\mu_x) = B_1 \end{aligned}\right\} \tag{47c}$$

Now we see the effect of $\hat{\theta}_t$, the time-reversal operator, on $\langle e'v' | \mu \pm | e''v'' \rangle$ while maintaining the assumption that $|e'v'\rangle$ and $|e''v''\rangle$ are real basis functions. Then

$$\hat{\theta}_t \langle e'v' | \mu \pm | e''v'' \rangle = \langle e'v' | \mu \mp | e''v'' \rangle \tag{48a}$$

We see that the effect is not quite clear in the sense that we do not know whether the right hand side of (48a) is $\langle e'v' | \mu \pm | e''v'' \rangle$ or $-\langle e'v' | \mu \pm | e''v'' \rangle$. To decide it, we go on to see the effect of at least

two of the symmetry elements of the group. Using more than two elements of the group will be redundant for they do not provide additional information in this regard. Thus

$$\hat{\sigma}_v(xz)\langle e'v'|\mu_\pm|e''v''\rangle = \langle e'v'|\mu_\mp|e''v''\rangle \qquad (48b)$$

$$\hat{\sigma}_v(yz)\langle e'v'|\mu_\pm|e''v''\rangle = \langle e'v'|\mu_\mp|e''v''\rangle \qquad (48c)$$

Since (48b) and (48c) each must be equal to $\langle e'v'|\mu_\pm|e''v''\rangle$ to be non-vanishing, we obtain

$$\langle e'v'|\mu_\pm|e''v''\rangle = \langle e'v'|\mu_\mp|e''v''\rangle \neq 0 \qquad (48d)$$

Use of (48d) in (48a) gives

$$\hat{\theta}_t\langle e'v'|\mu_\pm|e''v''\rangle = \langle e'v'|\mu_\pm|e'''v''\rangle = \text{REAL}. \qquad (48e)$$

(48e) suggests that the dipole moment component is μ_x corresponding to the vibronic integral. Also, from (34) we find that

$$\mu_x = (\mu_+ + \mu_-)/\sqrt{2} \qquad (49a)$$

$$\mu_y = (\mu_+ - \mu_-)/\sqrt{2} \qquad (49b)$$

Then from (48d), (49a) and (49b) we find that

$$\begin{aligned}\langle e'v'|\mu_\pm|e''v''\rangle &= \langle e'v'|\mu_\mp|e''v''\rangle \\ &= \frac{1}{\sqrt{2}}\langle e'v'|\frac{\mu_+ + \mu_-}{\sqrt{2}}|e''v''\rangle \\ &= \frac{1}{\sqrt{2}}\langle e'v'|\mu_x|e''v''\rangle \\ &= \frac{1}{\sqrt{2}}\langle \mu_x\rangle \end{aligned} \qquad (50)$$

Then using (50) in (41), we obtain the line strengths

$$[S]^{J''}_{J'} = \frac{1}{6}\langle \mu_x \rangle^2 \left| \sum_{K''} \left\{ a^{\tau''}_{K''} a^{\tau'}_{K''-1} \langle J'K''-1 | f_+ | J''K'' \rangle + a^{\tau''}_{K''} a^{\tau'}_{K''+1} \langle J'K''+1 | f_- | J''K'' \rangle \right\} \right|^2 \quad (51)$$

and the corresponding relative intensities as follows.

$$[I]^{J''}_{J'} = \nu g_{J''} (2J''+1) e^{-E/T^*} \cdot \frac{1}{6}\langle \mu_x \rangle^2 \left| \sum_{K''} \left\{ a^{\tau''}_{K''} a^{\tau'}_{K''-1} \langle J'K''-1 | f_+ | J''K'' \rangle + a^{\tau''}_{K''} a^{\tau'}_{K''+1} \langle J'K''+1 | f_- | J''K'' \rangle \right\} \right|^2 \quad (52)$$

Here again the values for the rotation matrices are given in TABLE 2.

CASE (4): $\Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = B_2$

From (31) we obtain

$$\Gamma(\psi'_r) \times \Gamma(\psi''_r) = B_1 \quad (53a)$$

so, from the group theory, the only possible transitions are

$$A_1 \longleftrightarrow B_1 \quad \text{and} \quad A_2 \longleftrightarrow B_2$$

Also the requirement

$$\Gamma(\mu_\alpha) = B_2 \quad (53b)$$

shows that transitions are governed by μ_y, the y-component of the dipole moment in the molecular-fixed frame. Thus the allowed transitions between rotational

states are

$$\left.\begin{array}{l} A_1 \leftrightarrow B_1 \quad \text{and} \quad A_2 \leftrightarrow B_2 \\ \text{FOR} \quad \Gamma(\psi'_{ev}) \times \Gamma(\psi''_{ev}) = B_2 \quad \text{AND} \quad \Gamma(\mu_y) = B_2 \end{array}\right\} \quad (53c)$$

Now, assuming as before, the vibronic basis functions to be real, the time reversal operation on vibronic integral gives

$$\hat{\theta}_t \langle e'v' | \mu_\pm | e''v'' \rangle = \langle e'v' | \mu_\mp | e''v'' \rangle \quad (54a)$$

(54a) here is the same as (48a) despite the fact that the combination of vibronic states is different than that in (48a). Again we need to know the symmetry properties of the integral $\langle e'v' | \mu_\pm | e''v'' \rangle$.

Thus for the allowed transitions (53c) in this case, we have

$$\hat{\sigma}_v(xz) \langle e'v' | \mu_\pm | e''v'' \rangle = -\langle e'v' | \mu_\mp | e''v'' \rangle \quad (54b)$$

$$\hat{\sigma}_v(yz) \langle e'v' | \mu_\pm | e''v'' \rangle = -\langle e'v' | \mu_\mp | e''v'' \rangle \quad (54c)$$

Since (54b) and (54c) each must be equal to $\langle e'v' | \mu_\pm | e''v'' \rangle$ in order to be nonvanishing, we obtain

$$\langle e'v' | \mu_\pm | e''v'' \rangle = -\langle e'v' | \mu_\mp | e''v'' \rangle \neq 0 \quad (54d)$$

Use of (54d) in (54a) gives

$$\hat{\theta}_t \langle e'v' | \mu_\pm | e''v'' \rangle = -\langle e'v' | \mu_\pm | e''v'' \rangle = \text{IMAGINARY} \quad (54e)$$

(54e) suggests that the transition moment involves μ_y, the y-component of the dipole moment in the molecular-fixed coordinates. In view of the relation (49a), (49b) and (54d), we find that

$$\begin{aligned}\langle e'v'|\mu_\pm|e''v''\rangle &= -\langle e'v'|\mu_\mp|e''v''\rangle \\ &= \tfrac{1}{2}\langle e'v'|(\mu_\pm+\mu_\pm)|e''v''\rangle \\ &= \tfrac{1}{2}\langle e'v'|(\mu_\pm-\mu_\mp)|e''v''\rangle \\ &= \pm\frac{i}{\sqrt{2}}\langle e'v'|\mu_y|e''v''\rangle = \pm\, i\frac{\langle\mu_y\rangle}{\sqrt{2}} \qquad (55)\end{aligned}$$

Then using (55) in (41), one obtains the relation of line strengths. Thus

$$[S]^{J''}_{J'} = \frac{\langle\mu_y\rangle^2}{6}\left|\sum_{K''}\left\{a^{\tau''}_{K''}\,a^{\tau'}_{K''-1}\langle J'K''-1|f_+|J''K''\rangle - a^{\tau''}_{K''}\,a^{\tau'}_{K''+1}\langle J'K''+1|f_-|J''K''\rangle\right\}\right|^2 \qquad (56)$$

and the relative intensities corresponding to (56) are

$$[I]^{J''}_{J'} = \nu g_{J''}(2J''+1)e^{-E/T^*}\frac{\langle\mu_y\rangle^2}{6}\left|\sum_{K''}\left\{a^{\tau''}_{K''}\,a^{\tau'}_{K''-1}\langle J'K''-1|f_+|J''K''\rangle - a^{\tau''}_{K''}\,a^{\tau'}_{K''+1}\langle J'K''+1|f_-|J''K''\rangle\right\}\right|^2 \qquad (57)$$

Thus, it is possible to calculate all the energies and the corresponding relative intensities.

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3. APPLICATION TO $\tilde{C}^1B_1$, AND $\tilde{D}^1A_1$ BANDS OF WATER

3.1: CALCULATIONS OF EFFECTIVE ROTATIONAL CONSTANTS

The aim of this chapter is to apply the theory, developed in Chapter 2, to the representative molecules of symmetry C_{2v} so that the results of this theory and those obtained on the basis of our theory in Chapter 4 may be compared not only with each other but also with the experimentally observed ones.

Here we have considered H_2O and D_2O for the studies of rotation-electronic energies and relative transitions from the ground rotation-electronic states $\tilde{X}^1A_1$, to the $3p$- complex Rydberg state . We define the $3p$-orbitals, corresponding to the $3p$-complex state , by the orbital functions $|x\rangle$, $|y\rangle$ and $|z\rangle$ as follows:

$$|x\rangle = \frac{1}{\sqrt{2}}\left[|\Lambda=+1\rangle - |\Lambda=-1\rangle\right] \equiv \frac{1}{\sqrt{2}}\left[|1\rangle - |-1\rangle\right] \quad (58a)$$

$$|y\rangle = \frac{1}{\sqrt{2}}\left[|\Lambda=+1\rangle + |\Lambda=-1\rangle\right] \equiv \frac{1}{\sqrt{2}}\left[|1\rangle + |-1\rangle\right] \quad (58b)$$

$$|z\rangle = |\Lambda=0\rangle \equiv |0\rangle \quad (58c)$$

where $\Lambda = 0, \pm 1$ are the projections (taken along the molecule -fixed z-axis) of the orbital angular momentum quantum number $L = 1$. The axes in Eqs. (58) have been chosen such that the orbital functions $|x\rangle$, $|y\rangle$ and $|z\rangle$ transform like the x , y and z components respectively of an ordinary polar vector as can be seen from the following explanation.

If J represents the total angular momentum quantum number and K its projections along the z-axis in the molecule -fixed frame then, according to Hougen [9] , the total angular momentum wavefunctions $|JK\rangle$ for integral quantum numbers transform according to Eqs. (20). Note that the improper rotations were obtained by writing $\hat{Q} = \hat{R}\hat{i}$ in which $\hat{Q}$ is the improper rotation, $\hat{R}$ the proper rotation and $\hat{i}$ is the inversion operation (all referred to the molecule -fixed frame); improper rotations are also accompanied by the space-fixed inversion operation and thus the effect of $\hat{Q}$ is identical to that of $\hat{R}$. The effect of the $\hat{\sigma}(xz)$ and $\hat{\sigma}(yz)$ operations are thus given by the $\hat{C}_{2y}$ and $\hat{C}_{2x}$ operations respectively.

Electronic orbital functions transform under rotations in the same way as the total angular momentum but the orbital functions are also affected by spatial transformations. Therefore, the effect of inversion $\hat{i}$ in the molecule -fixed frame must be taken into consideration in the case of improper rotations. For $\hat{i}$, we know that the spherical harmonics for a single electron are altered by

$$\hat{i}|l\lambda\rangle = (-1)^{l}|l\lambda\rangle \qquad (59)$$

where l is the electronic orbital quantum number and λ is one of the possible projections of l . Then assuming $|L\Lambda\rangle$ to represent some linear combination of

products of orbital states for each electron, we see that

$$\hat{i}\,|L\Lambda\rangle = (-1)^{\sum_k \ell_k}\,|L\Lambda\rangle \tag{60}$$

where the index k runs over all the values of ℓ corresponding to different states of the electrons under consideration. Recalling that $\hat{Q} = \hat{R}\,\hat{i}$ where the effect of $\hat{R}$ on $|L\Lambda\rangle$ is identical to that given for $|JK\rangle$ by Eqs. (20) we now see that

$$\hat{C}_{2z}\,|L\Lambda\rangle = (-1)^{\Lambda}\,|L\Lambda\rangle \tag{61a}$$

$$\hat{\sigma}_v(xz)\,|L\Lambda\rangle = (-1)^{L-\Lambda+\sum_k \ell_k}\,|L-\Lambda\rangle \tag{61b}$$

$$\hat{\sigma}_v(yz)\,|L\Lambda\rangle = (-1)^{L+\sum_k \ell_k}\,|L-\Lambda\rangle \tag{61c}$$

In practice, we are concerned with states arising from a single electron. In such a case $L = \sum_k \ell_k \equiv \ell$ and our Eqs. (61) simplify to

$$\hat{C}_{2z}\,|L\Lambda\rangle = (-1)^{\Lambda}\,|L\Lambda\rangle \tag{62a}$$

$$\hat{\sigma}_v(xz)\,|L\Lambda\rangle = (-1)^{\Lambda}\,|L-\Lambda\rangle \tag{62b}$$

$$\hat{\sigma}_v(yz)\,|L\Lambda\rangle = |L-\Lambda\rangle \tag{62c}$$

Using the transformations given by Eqs. (62) on the p-orbital functions defined by Eqs. (58), we find that the functions $|x\rangle$, $|y\rangle$ and $|z\rangle$ transform like the x, y, z components respectively of an ordinary polar vector. Then $|x\rangle$, $|y\rangle$ and $|z\rangle$ have the symmetry

species B_1, B_2 and A_1 respectively. In the ground state, the molecular core of H_2O (or D_2O) is of symmetry B_1 while the valence electron is a b_1 -electron. Since a transition from the ground state to the excited $3p$-orbital states is brought about by the promotion of a b_1 electron, the molecular core in both the ground and the excited state is of symmetry $^1B_1$. The overall symmetry in each case is the product of the core symmetry and that of the electronic state symmetry. This yields the overall symmetry $^1B_1 \times {}^1B_1 = {}^1A_1$ for the ground state while for the components of the $3p$- orbital, $^1B_1 \times (^1B_1, {}^1B_2, {}^1A_1) = (^1A_1, {}^1A_2, {}^1B_1)$ correspond to the orbital functions ($|x\rangle$, $|y\rangle$, $|z\rangle$).

In order to carry out the numerical calculations of energies of the rotational states of H_2O and D_2O in different electronic states, one needs to know the numerical values of the rotational constants for each molecule in the ground rotation-electronic states $\tilde{X}\,{}^1A_1$, and the excited rotation-electronic states $\tilde{C}\,{}^1B_1$, and $\tilde{D}^1A_1$. The rotational constants of the $\tilde{X}^1A_1$ state of H_2O and D_2O (Herzberg [7] and Benedict et.al.[2]) and the effective rotational constants of the $\tilde{C}^1B_1$ rotation-electronic states of H_2O and D_2O (Johns [11]) are known. However, in order to obtain the rotation-electronic energies in the $\tilde{D}^1A_1$ state of H_2O (or D_2O), one needs to know the numerical values of the effective

rotational constants corresponding to the $\tilde{D}\,^1A_1$ states of these molecules. Therefore, we need to establish the mathematical relations which connect the effective rotational constants A_{eff} , B_{eff} and C_{eff} to their corresponding deperturbed (or ℓ - uncoupled) rotational constants A, B and C, consistent with our choice of axes a , b, and c. We have chosen the b and c axes so that $b = z$ is the two-fold rotation axis and $c \equiv x$ is the axis perpendicular to the molecular plane, in accordance with the convention for an asymmetric-top molecule of C_{2v} symmetry.

To evaluate the relations for the effective rotational constants corresponding to the three rotation-electronic states, we consider the Hamiltonian

$$\hat{H} = \left\{ C\left(\hat{J}_x - \hat{L}_x\right)^2 + A\left(\hat{J}_y - \hat{L}_y\right) + B\left(\hat{J}_z - \hat{L}_z\right)^2 \right\} + \left\{ \mathcal{E}_x\left(1 - \hat{L}_x^2\right) + \mathcal{E}_y\left(1 - \hat{L}_y^2\right) + \mathcal{E}_z\left(1 - \hat{L}_z^2\right) \right\} \qquad (63)$$

where the first bracket represents the rotational Hamiltonian while the second bracket represents the non-rotating Hamiltonian. $\mathcal{E}_x$, $\mathcal{E}_y$ and $\mathcal{E}_z$ are the electronic energies for the states $|x\rangle$, $|y\rangle$ and $|z\rangle$ respectively. $\hat{J}_\alpha$ ($\alpha = x, y, z$) are the components of the total angular momentum $\hat{J}$, and $\hat{L}_\alpha$ ($\alpha = x, y, z$) are the components of the orbital angular momentum $\hat{L}$. It may be pointed out that the terms $\mathcal{E}_\alpha(1 - \hat{L}_\alpha^2$) are introduced in the Hamiltonian such that the resulting energies $\mathcal{E}_\alpha$ ($\alpha = x, y, z$)

corresponding to the three orbital electronic states do not interact with one another. The choice of $\mathcal{E}_\alpha(1-L_\alpha)$ is rather artificial because the wavefunctions of the three orbital electronic states considered in this work are such as to lead to the same electronic energies as would have been obtained by merely adding the electronic energies.

Rearrangement of Eq. (63) leads to the result

$$\hat{H} = \{\hat{H}_r + \hat{H}_{el} + (A+B+C)\} + \hat{H}_{re} \equiv \hat{H}_{diag} + \hat{H}_{re} \tag{64}$$

where

$$\hat{H}_r = A\hat{J}_y^2 + B\hat{J}_z^2 + C\hat{J}_x^2 \tag{65a}$$

$$\hat{H}_{el} = (\mathcal{E}_x - C)(1-\hat{L}_x^2) + (\mathcal{E}_y - A)(1-\hat{L}_y^2) + (\mathcal{E}_z - B)(1-\hat{L}_z^2) \tag{65b}$$

$$\hat{H}_{re} = -2A\hat{J}_y\hat{L}_y - 2B\hat{J}_z\hat{L}_z - 2C\hat{J}_x\hat{L}_x \tag{65c}$$

The Hamiltonians $\hat{H}_r$, $\hat{H}_{el}$ and $\hat{H}_{re}$ represent purely rotational, purely electronic and rotation-electronic interaction parts of $\hat{H}$ respectively. Note that $\hat{H}$ has the matrix elements that are purely diagonal in the electronic quantum numbers. The off-diagonal matrix elements, given by $\hat{H}_{re}$, may be treated as a perturbation.

The orbital electronic functions $|\alpha\rangle$ ($\alpha = x, y, z$) on being operated by the orbital angular momentum components $\hat{L}_\alpha$ ($\alpha = x, y, z$) behave as follows

$$\hat{L}_x|x\rangle = 0 \quad ; \quad \hat{L}_y|x\rangle = i|z\rangle \quad ; \quad \hat{L}_z|x\rangle = |y\rangle \tag{66a}$$

$$\hat{L}_x|y\rangle = |z\rangle \quad ; \quad \hat{L}_y|y\rangle = 0 \quad ; \quad \hat{L}_z|y\rangle = |x\rangle \tag{66b}$$

$$\hat{L}_x|z\rangle = |y\rangle \quad ; \quad \hat{L}_y|z\rangle = -i|x\rangle \quad ; \quad \hat{L}_z|z\rangle = 0 \tag{66c}$$

where $i \equiv \sqrt{-1}$. If we represent the rotation functions by $|R\rangle \equiv |JK\rangle$, then we can write the entire wavefunction as

$$|JK\alpha\rangle \equiv |R\alpha\rangle = |R\rangle|\alpha\rangle \tag{67}$$

for the rotation-electronic states. Thus, in view of Eqs. (67), we see from Eq. (64) that the matrix elements for a definite electronic state $|\alpha\rangle$, to second order, are

$$\langle R'\alpha|\hat{H}|R\alpha\rangle = \langle R'\alpha|\hat{H}_{diag}|R\alpha\rangle + \sum_{R'',\alpha''\neq\alpha} \frac{\langle R'\alpha|\hat{H}_{re}|R''\alpha''\rangle\langle R''\alpha''|\hat{H}_{re}|R\alpha\rangle}{\mathcal{E}^{(0)}_{R\alpha} - \mathcal{E}^{(0)}_{R''\alpha''}} \tag{68a}$$

Since the first-order contribution, given by $\langle R'\alpha|\hat{H}_{re}|R\alpha\rangle$ vanishes. The first term, $\langle R'\alpha|\hat{H}_{diag}|R\alpha\rangle$, gives the zero-order contribution to the total energy; that is,

$$\mathcal{E}^{(0)}_{R\alpha} = \langle R\alpha|\hat{H}_{diag}|R\alpha\rangle \tag{68b}$$

In Eq. (68a), we have assumed that the electronic spacing is much larger than the spacing of the rotational energy levels. That is,

$$\mathcal{E}^{(0)}_{R\alpha} - \mathcal{E}^{(0)}_{R''\alpha''} \simeq \mathcal{E}^{(0)}_{\alpha} - \mathcal{E}^{(0)}_{\alpha''} \tag{68c}$$

This approximation is reasonable because the purely rotational separations involving the rotational constants

A, B and C, are insignificant when compared with the electronic separations. The first term of Eq. (68a) has the matrix elements

$$\langle R'\alpha | \hat{H}_{diag} | R\alpha \rangle = \langle R' | \hat{H}_r | R \rangle + \left[\langle \alpha | \hat{H}_{el} | \alpha \rangle + (A+B+C) \right] \delta_{R'R} \quad (69)$$

If we define the effective electronic energy contribution by

$$\mathcal{E}_{eff_\alpha} = \left[\langle \alpha | \hat{H}_{el} | \alpha \rangle + (A+B+C) \right] \quad (70)$$

we can write Eq. (69) in the form

$$\langle R'\alpha | \hat{H}_{diag} | R\alpha \rangle = \langle R' | \hat{H}_r | R \rangle + \mathcal{E}_{eff_\alpha} \delta_{R'R} \quad (71)$$

Then, the zero-order energy contribution is

$$\mathcal{E}^{(0)}_{R\alpha} = \langle R | \hat{H}_r | R \rangle + \mathcal{E}_{eff_\alpha} \quad (72)$$

where we find, using Eqs. (66), that

$$\mathcal{E}_{eff_x} = (\mathcal{E}_x - C) + (A+B+C) \quad (73a)$$

$$\mathcal{E}_{eff_y} = (\mathcal{E}_y - A) + (A+B+C) \quad (73b)$$

$$\mathcal{E}_{eff_z} = (\mathcal{E}_z - B) + (A+B+C) \quad (73c)$$

We note from (72) that

$$\mathcal{E}^{(0)}_{R\alpha} - \mathcal{E}^{(0)}_{R''\alpha''} = \left[\mathcal{E}_{eff_\alpha} - \mathcal{E}_{eff_{\alpha''}} \right] + \left[\langle R | \hat{H}_r | R \rangle - \langle R'' | \hat{H}_r | R'' \rangle \right] \quad (74)$$

Because of our earlier assumption that the rotational states are very closely spaced compared to the electronic states we can ignore the second bracket on the right hand side of Eq. (74). Then from Eqs. (74) and (69), we have

$$\mathcal{E}^{(0)}_{R\alpha} - \mathcal{E}^{(0)}_{R''\alpha''} \simeq \mathcal{E}^{(0)}_{\alpha} - \mathcal{E}^{(0)}_{\alpha''} \equiv \mathcal{E}_{eff_\alpha} - \mathcal{E}_{eff_{\alpha''}} \tag{75}$$

Thus, using the result in Eq. (75) we can rewrite Eq. (68a) as follows

$$\langle R'\alpha|\hat{H}|R\alpha\rangle = \langle R'\alpha|\hat{H}_{diag}|R\alpha\rangle + \sum_{R'',\alpha''\neq\alpha} \frac{\langle R'\alpha|\hat{H}_{re}|R''\alpha''\rangle\langle R''\alpha''|\hat{H}_{re}|R\alpha\rangle}{\mathcal{E}_{eff_\alpha} - \mathcal{E}_{eff_{\alpha''}}} \tag{76}$$

Since for the states $|x\rangle$, $|y\rangle$ and $|z\rangle$, we have

$$\langle R'x|\hat{H}_{re}|R''y\rangle\langle R''y|\hat{H}_{re}|Rx\rangle = \langle R'y|\hat{H}_{re}|R''x\rangle\langle R''x|\hat{H}_{re}|Ry\rangle = 4B^2\langle R'|\hat{J}_z^2|R\rangle \tag{77a}$$

$$\langle R'x|\hat{H}_{re}|R''z\rangle\langle R''z|\hat{H}_{re}|Rx\rangle = \langle R'z|\hat{H}_{re}|R''x\rangle\langle R''x|\hat{H}_{re}|Rz\rangle = 4A^2\langle R'|\hat{J}_y^2|R\rangle \tag{77b}$$

$$\langle R'y|\hat{H}_{re}|R''z\rangle\langle R''z|\hat{H}_{re}|Ry\rangle = \langle R'z|\hat{H}_{re}|R''y\rangle\langle R''y|\hat{H}_{re}|Rz\rangle = 4C^2\langle R'|\hat{J}_x^2|R\rangle \tag{77c}$$

we get from Eqs. (71), (76) and (77)

$$\langle R'x|\hat{H}|Rx\rangle = \langle R'|\hat{H}_r|R\rangle + \mathcal{E}_{eff_x}\delta_{RR'} + \frac{4B^2\langle R'|\hat{J}_z^2|R\rangle}{\mathcal{E}_{eff_x} - \mathcal{E}_{eff_y}} + \frac{4A^2\langle R'|\hat{J}_y^2|R\rangle}{\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z}} \tag{78a}$$

$$\langle R'y|\hat{H}|Ry\rangle = \langle R'|\hat{H}_r|R\rangle + \mathcal{E}_{eff_y}\delta_{RR'} + \frac{4B^2\langle R'|\hat{J}_z^2|R\rangle}{\mathcal{E}_{eff_y} - \mathcal{E}_{eff_x}} + \frac{4C^2\langle R'|\hat{J}_x^2|R\rangle}{\mathcal{E}_{eff_y} - \mathcal{E}_{eff_z}} \tag{78b}$$

$$\langle R'z|\hat{H}|Rz\rangle = \langle R'|\hat{H}_r|R\rangle + \mathcal{E}_{eff_z}\delta_{RR'} + \frac{4A^2\langle R'|\hat{J}_y^2|R\rangle}{\mathcal{E}_{eff_z} - \mathcal{E}_{eff_x}} + \frac{4C^2\langle R'|\hat{J}_x^2|R\rangle}{\mathcal{E}_{eff_z} - \mathcal{E}_{eff_y}} \tag{78c}$$

Collecting coefficients of $\hat{J}_x^2$, $\hat{J}_y^2$ and $\hat{J}_z^2$ with the aid of Eq. (65a), we find that

$$\langle R'\alpha|\hat{H}|R\alpha\rangle = \langle R'|(\hat{H}_{eff})_\alpha|R\rangle + \mathcal{E}_{eff_\alpha}\delta_{RR'} \quad (79)$$

where

$$(\hat{H}_{eff})_\alpha = (A_{eff}\hat{J}_y^2 + B_{eff}\hat{J}_z^2 + C_{eff}\hat{J}_x^2)_\alpha \quad ; \quad (\alpha = x, y, z) \quad (80)$$

and the effective rotational constants for each state $|\alpha\rangle \equiv |x\rangle$, $|y\rangle$ and $|z\rangle$ are given by the following equations.

For electronic state $|x\rangle$:

$$A_{eff} = A\left[1 + \frac{4A}{\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z}}\right] \quad (81a)$$

$$B_{eff} = B\left[1 + \frac{4B}{\mathcal{E}_{eff_x} - \mathcal{E}_{eff_y}}\right] \quad (81b)$$

$$C_{eff} = C \quad (81c)$$

For electronic state $|y\rangle$:

$$A_{eff} = A \quad (82a)$$

$$B_{eff} = B\left[1 + \frac{4B}{\mathcal{E}_{eff_y} - \mathcal{E}_{eff_x}}\right] \quad (82b)$$

$$C_{eff} = C\left[1 + \frac{4C}{\mathcal{E}_{eff_y} - \mathcal{E}_{eff_z}}\right] \quad (82c)$$

For electronic state $|z\rangle$:

$$A_{eff} = A\left[1 + \frac{4A}{\mathcal{E}_{eff_z} - \mathcal{E}_{eff_x}}\right] \quad (83a)$$

$$B_{eff} = B \quad (83b)$$

$$C_{eff} = C\left[1 + \frac{4C}{\mathcal{E}_{eff_z} - \mathcal{E}_{eff_y}}\right] \quad (83c)$$

On comparing the results given here by Eqs.(81), (82) and (83) with Eqs. (6x), (6y) and (6z) given by Creutzberg and Hougen [5] for the analogous spin problem, later adapted by Johns [11] for this orbital problem, we find the following correspondence between the spin state functions and the orbital electronic functions.

TABLE 3

CORRESPONDENCE BETWEEN THE SPIN FUNCTIONS (ADOPTED EARLIER) AND ELECTRONIC FUNCTIONS

Electronic State	J.W.C. JOHNS	PRESENT WORK		Selection Rule From Symmetry (Allowed/ Forbidden)
	Spin Function	Electronic Function	Component of Dipole Active in Transition	
$\tilde{C}\,{}^1B_1$	$\|x\rangle$	$\|z\rangle$	μ_x	Allowed
$\tilde{D}\,{}^1A_1$	$\|y\rangle$	$\|x\rangle$	μ_z	Allowed
${}^1A_2$	$\|z\rangle$	$\|y\rangle$	μ_y	Forbidden

The difference arises because of the fact that the components of orbital functions behave like the ordinary polar vectors rather than the components of axial vectors; the latter is the characteristic of the spin functions. Also we have chosen x, y, z axes of principal moments of inertia as c, a, b respectively; which is different from the earlier choice of b, c, a respectively as is evident by comparing FIG. 3 (a) and 3(b).

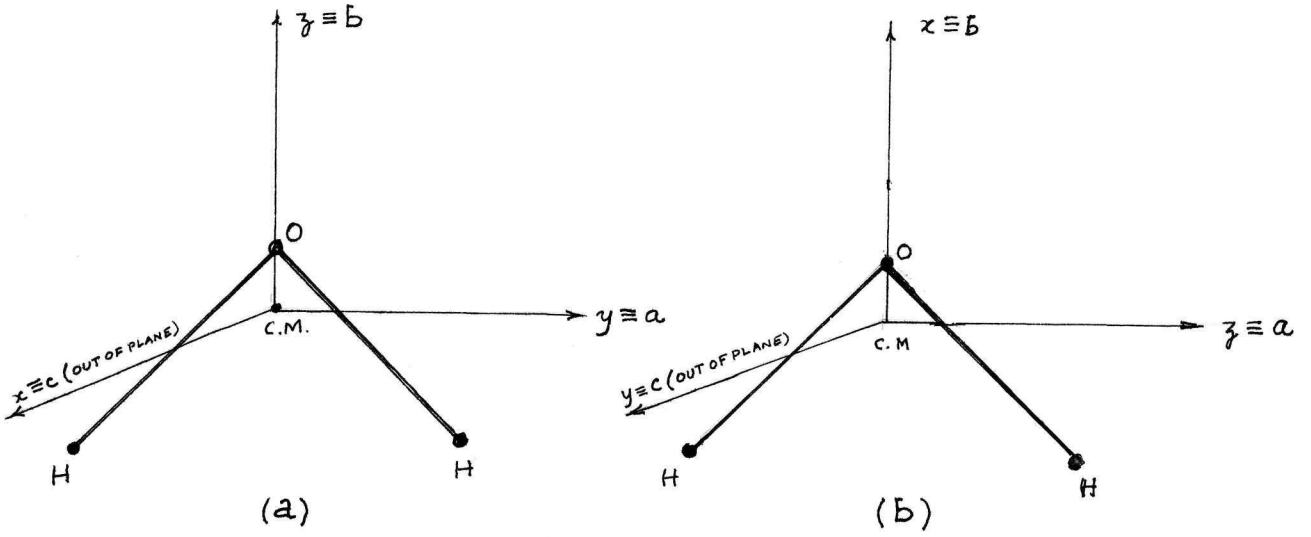

FIG. 3 . (a) Represents our choice of axes

(b) Represents choice of axes adopted by Johns for H_2O molecules.

Therefore, by replacing in Eqs. (6x), (6y) and (6z) of Creutzberg and Hougen

$$\left.\begin{array}{lll} E_x \longrightarrow \mathcal{E}_{eff_z} \; ; & E_y \longrightarrow \mathcal{E}_{eff_x} \; ; & E_z \longrightarrow \mathcal{E}_{eff_y} \\ A \longrightarrow B \; ; & B \longrightarrow C \; ; & C \longrightarrow A \end{array}\right\} \qquad (84)$$

Eq. (6x), also given by Johns [11] , reduces to Eq. (83); Eq. (6y) reduces to Eq. (81) and Eq. (6z) to Eq. (82). Notice that we must use the effective values of electronic energy $\mathcal{E}_{eff_\alpha}$ ($\alpha = x, y, z$) in the expressions (81), (82) and (83) instead of the "deperturbed" values, E_α , used by Creutzberg and Hougen [5] . Note that Eq. (82) is not needed since the transitions to the $|y\rangle$ electronic state (CASE (2) of Chapter 2) are forbidden.

To calculate the effective rotational constants for the rotational band in the $\tilde{D}^1A_1$ electronic state (that is, $|x\rangle$ state) the following method has been adopted.

(1): The experimental values of effective rotational constants A_{eff}, B_{eff} and C_{eff} for $\tilde{C}^1B_1$ rotational-electronic states of H_2O (or D_2O) (Johns [11]) are used in Eqs. (83) and the corresponding deperturbed rotational constants A, B and C obtained, where the differences in the effective electronic energies ($\mathcal{E}_{eff_z} - \mathcal{E}_{eff_x}$) and ($\mathcal{E}_{eff_z} - \mathcal{E}_{eff_y}$) used here are given by Johns [11]. Thus,

For H_2O:

$$\left.\begin{aligned} \mathcal{E}_{eff_z} - \mathcal{E}_{eff_x} &= -1434 \ cm^{-1} \\ \mathcal{E}_{eff_z} - \mathcal{E}_{eff_y} &= 3587 \ cm^{-1} \end{aligned}\right\} \qquad (85a)$$

For D_2O:

$$\left.\begin{aligned} \mathcal{E}_{eff_z} - \mathcal{E}_{eff_x} &= -1323 \ cm^{-1} \\ \mathcal{E}_{eff_z} - \mathcal{E}_{eff_y} &= 2198 \ cm^{-1} \end{aligned}\right\} \qquad (85b)$$

The deperturbed (ℓ - uncoupled) rotational constants for H_2O and D_2O so obtained are listed in TABLE 4.

TABLE 4

ROTATIONAL CONSTANTS AND BAND ORIGINS OF $\tilde{X}\,^1A_1$, $\tilde{C}\,^1B_1$ AND $\tilde{D}\,^1A_1$ STATES OF H_2O AND D_2O.

I Notation	II Constants for H_2O (cm^{-1})	III Constants for D_2O (cm^{-1})
	$\tilde{X}\,^1A_1$ States	$\tilde{X}\,^1A_1$ States
ν_o	0.0	0.0
A	27.877	15.38
B	14.512	7.27
C	9.285	4.85
	$\tilde{C}\,^1B_1$ States	$\tilde{C}\,^1B_1$ States
ν_o'	80624.7	80751.9
A_{eff}	25.90	14.64
B_{eff}	12.64	6.31
C_{eff}	8.55	4.42
	$\tilde{D}\,^1A_1$ States	$\tilde{D}\,^1A_1$ States
ν_o'	82058.7	82074.9
A_{eff}	30.30 (2537)*	16.06 (2387)*
B_{eff}	12.76 (7281)*	6.355(2325)*
C_{eff}	8.47	4.38
	For Deperturbed States	For Deperturbed States
A'	28.10	15.35
B'	12.64	6.31
C'	8.47	4.38

* NOTE THAT THE NUMBERS APPEARING IN SMALL BRACKETS INDICATE ADDITIONAL DIGITS UP TO SIX OR SEVEN DECIMAL PLACE ACCURACY FOR THE EFFECTIVE ROTATIONAL CONSTANTS IN $\tilde{D}\,^1A_1$ STATES, USED IN CALCULATIONS.

Johns[11] has obtained the same results for A, B and C for H_2O and D_2O using Eq. (6x) of Creutzberg and Hougen, as expected, because a difference in the choice of axes should not affect the rotational constants.

(2): The deperturbed rotational constants obtained in step (1) (given in TABLE 4) and the differences in various orbital states (obtained from Eqs.(85)) for H_2O and D_2O

For H_2O:

$$\left.\begin{aligned} &\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z} = 1434\ cm^{-1} \\ &\mathcal{E}_{eff_x} - \mathcal{E}_{eff_y} = (\mathcal{E}_{eff_z} - \mathcal{E}_{eff_y}) - (\mathcal{E}_{eff_z} - \mathcal{E}_{eff_x}) = 5021\ cm^{-1} \end{aligned}\right\} \quad (86a)$$

For D_2O:

$$\left.\begin{aligned} &\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z} = 1323\ cm^{-1} \\ &\mathcal{E}_{eff_x} - \mathcal{E}_{eff_y} = (\mathcal{E}_{eff_z} - \mathcal{E}_{eff_y}) - (\mathcal{E}_{eff_z} - \mathcal{E}_{eff_x}) = 3521\ cm^{-1} \end{aligned}\right\} \quad (86b)$$

are used for H_2O and D_2O to calculate their effective rotational constants A_{eff}, B_{eff} and C_{eff} for the rotational band of the electronic state $\tilde{D}\ ^1A_1$. The results thus obtained are given in TABLE 4.

The effective rotational constants for H_2O and D_2O for the bands $\tilde{C}\ ^1B_1$ and $\tilde{D}\ ^1A_1$ are used in calculating the energies of rotational levels as described in Section 3.3.

3.2 CALCULATIONS OF BAND ORIGINS OF $\tilde{D}\ ^1A_1$ BANDS OF H_2O AND D_2O

Since the numerical values of the separation between

the electronic states $|x\rangle$ ($\equiv \tilde{D}\ ^1A_1$) and $|z\rangle$ ($\equiv \tilde{C}\ ^1B_1$), and also the band origins of the $|z\rangle$ ($\equiv \tilde{C}\ ^1B_1$) electronic state of H_2O and D_2O are known (Johns [11] and [2]), the band origin of the $\tilde{D}\ ^1A_1$ electronic state for each H_2O and D_2O have been evaluated as follows.

For H_2O:

The band origin of the $\tilde{C}\ ^1B_1$ state is

$$\nu_o'(\tilde{C}\ ^1B_1) \equiv \mathcal{E}_{eff_z} = 80624.7 \text{ cm}^{-1}$$

and since

$$\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z} = 1434 \text{ cm}^{-1}$$

the band origin of the $\tilde{D}\ ^1A_1$ state of H_2O is

$$\nu_o'(\tilde{D}\ ^1A_1) \equiv \mathcal{E}_{eff_x} = 82058.7 \text{ cm}^{-1}$$

For D_2O:

The band origin of the $\tilde{C}\ ^1B_1$ state is

$$\nu_o'(\tilde{C}\ ^1B_1) \equiv \mathcal{E}_{eff_z} = 80751.9 \text{ cm}^{-1}$$

and since

$$\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z} = 1323 \text{ cm}^{-1}$$

the band origin of the $\tilde{D}\ ^1A_1$ state of D_2O is

$$\nu_o'(\tilde{D}\ ^1A_1) \equiv \mathcal{E}_{eff_x} = 82074.9 \text{ cm}^{-1}$$

All these results are given in TABLE 4.

3.3 COMPUTATIONAL DETAILS OF ENERGIES

In order to carry out the numerical calculations of energies of the rotational states of H_2O and D_2O a computer programme has been developed which uses Eq.(17) to evaluate and store in the computer memory the matrix elements of a $(2J+1) \times (2J+1)$ matrix for each of the rotational quantum numbers from $J = 0$ through $J = 11$. The matrix so obtained for each single rotational quantum number J is diagonalized using a subroutine. The eigenvalues (which are merely the rotational energies) and their corresponding eigenvectors have been generated. The energies are rearranged in order of decreasing energy for each rotational quantum number J to facilitate the assignment of the label τ to each energy state. Thus, for $J = 2$, the energy levels have been identified by $J_\tau = 2_2, 2_1, 2_0, 2_{-1}$ and 2_{-2}, arranged in decreasing order of energy; there being $(2J + 1)$ energy states for a single J. In this way the rotational energies of the ground electronic state $\tilde{X}\,^1A_1$ and those of the excited states $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$, have been calculated using the ground state rotational constants and the effective rotational constants for the bands $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$. The constants are given in TABLE 4. The values of band origins $\nu_o' = 80624.7\ cm^{-1}$ and $\nu_o' = 82058.7\ cm^{-1}$ for $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$ electronic bands of H_2O respectively are added to the rotational

energies calculated above for H_2O so as to obtain the true energies of the rotation-electronic states. Similarly, for D_2O the band origins $\nu_o' = 80751.9\ cm^{-1}$ and $\nu_o' = 82074.9\ cm^{-1}$ are added to the rotational energies of the $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$ electronic bands respectively to obtain the true rotation-electron energies. Since both H_2O and D_2O are considered as rigid rotors in the ground electronic state $\tilde{X}\,^1A_1$, where the zero point energy of molecular vibration is ignored, the band origin is assigned a zero frequency ($\nu_o = 0$). The computed values of energies for the rotational states of the electronic bands $\tilde{X}\,^1A_1$, $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$, for H_2O and D_2O are given in TABLES II.1 and II.2 , respectively (APPENDIX II) up to the rotational quantum number $J = 11$.

3.4 THE NUCLEAR STATISTICAL WEIGHT

Since the transition intensities are affected by the nuclear spin of the nuclei in a molecule, we have considered their role in our calculations of relative intensities.

The eigenfunctions of homonuclear molecules are categorized as symmetric or antisymmetric depending on whether or not the eigenfunctions remain invariant on interchanging the coordinates of the nuclei. Let I be the nuclear spin of each nucleus, then if the identical nuclei are Bosons, there are $(I + 1).(2I + 1)$

symmetric and I.(2I + 1) antisymmetric eigenfunctions of the molecule with respect to interchange of nuclei. The reverse is true of Fermions, where the weight of antisymmetric states is (I + 1).(2I + 1) and that of symmetric ones is I.(2I + 1). Then the ratio, ξ , of the weights of symmetric to antisymmetric states in case of Bosons or the weights of antisymmetric to symmetric states in the case of Fermions, is given by

$$\xi = \frac{(I+1)}{I} = \left(\frac{\text{Symmetric States}}{\text{Antisymmetric States}}\right)_{\text{Bosons}} = \left(\frac{\text{Antisymmetric States}}{\text{Symmetric States}}\right)_{\text{Fermions}} \tag{87}$$

Thus for an H_2O molecule, since the exchange of position coordinates occurs between the two H - atoms, each of nuclear spin I = 1/2 (in units of $\hbar$), $s : a = 1 : 3$ while for a D_2O molecule in which deuterons are the Bosons, with nuclear spin I = 1, $s : a = 2 : 1$. Here s and a denote symmetric state and antisymmetric state respectively. Thus the statistical weight of an antisymmetric state is three times that of a symmetric state in H_2O whereas the weight of a symmetric state is twice that of an antisymmetric state in D_2O. Consequently, the intensity ratios will be 1 : 3 in H_2O and 2 : 1 in D_2O for $s : a$.

Now a $\hat{C}_{2z}$ operation gives a pure exchange of two nuclei. Then from the character table of C_{2V} point group (APPENDIX I) we see that A_1 and A_2 are each of

character $+1$ while B_1 and B_2 each has a character -1 under $\hat{C}_{2z}$ operation. Thus energy levels of species A_1, A_2 are symmetric while B_1, B_2 are anti-symmetric. Also the $\hat{\sigma}(yz)$ operation gives pure inversion so A_1, B_1 are of + parity and A_2, B_1 are of - parity. Thus, we can summarize our results as follows:

Species	Parity	S/a	Statistical Weight H_2O	Statistical Weight D_2O
A_1	+	S	1	2
A_2	-	S	1	2
B_1	-	a	3	1
B_2	+	a	3	1

3.5 COMPUTATIONAL DETAILS OF RELATIVE TRANSITION INTENSITIES.

The numerical computation has been carried out for two cases of transitions that are permitted by the symmetry requirement of the matrix elements. The permissible cases are

(i) $\tilde{X}^1A_1$ - $\tilde{C}^1B_1$ Transitions (Case (3) of Chapter 2).

(ii) $\tilde{X}^1A_1$ - $\tilde{D}^1A_1$ Transitions (Case (1) of Chapter 2).

The computational details for each case are exactly the same except for the difference in the subroutine which changes the symmetry codes of the upper levels appropriate to the bands involved in the transitions. For example, for the Case (i) which involves a transition between the rotational states of $\tilde{X}^1A_1$ and $\tilde{C}^1B_1$

electronic states, the only possible transitions between the rotational states (identified by their rotational symmetry species) are

$$A_1 \leftrightarrow B_2 \quad \text{and} \quad A_2 \leftrightarrow B_1$$

where the dipole component active in the transitions is μ_x which has the symmetry species $\Gamma(\mu_x) = B_1$. Similarly, for the case (ii) which involves the transitions between the bands $\tilde{X}\,^1A_1$ and $\tilde{D}\,^1A_1$, the possible combinations of rotational states are

$$A_1 \leftrightarrow A_2 \quad \text{and} \quad B_1 \leftrightarrow B_2$$

where in this case, the dipole component μ_z is active. The symmetry species is $\Gamma(\mu_z) = A_1$.

In each case, eigenvalues and eigenvectors are calculated for both the ground rotation-electronic states $\tilde{X}^1A_1$ and the excited electronic states $\tilde{C}^1B_1$ (or $\tilde{D}^1A_1$ in the case (ii)) and stored in the computer memory as was done in section 3.3. By calling a subroutine, each energy level is assigned a symmetry species (in the form of a code) consistent with the criteria established earlier (in Chapter 2, TABLE 1). At any instant, the symmetry codes so assigned to the energy states are stored for a given quantum number $J = J''$ of rotation in the $\tilde{X}\,^1A_1$ state and for $J' = J''-1$, J'' and $J''+1$ in the excited electronic state $\tilde{C}^1B_1$ (or $\tilde{D}^1A_1$). Thus, for example, in our case, we reserved the code 1

to represent the symmetry species A_1; 2 for A_2; 3 for B_1 and 4 for B_2. Subject to the allowed combination of states in transitions, the symmetry codes of the excited states for $J' = J'' - 1$, J'' and $J'' + 1$, stored earlier, are changed only to those of initial states for which combinations of states are allowed. That is, if the transitions $A_1 \leftrightarrow B_2$ and $A_2 \leftrightarrow B_1$ are allowed (say), the codes for the upper state species A_1, A_2, B_1 and B_2 must be changed to those of B_2, B_1, A_2 and A_1 respectively. This is done by calling a subroutine consistent with the selection rules. This technique, in effect, assigns the same code to those initial and final states which are permitted to combine by the selection rule. Thus, whenever the codes in the initial state and the final state match, the programme allows one to calculate the line strength and the relative transition intensity using (51) and (52) respectively for the $\tilde{C}^1B_1$ electronic band and (45a) and (45b) for the rotational transitions to the $\tilde{D}^1A_1$ electronic band. The nuclear statistical weight is attached to the relative intensity as described earlier in Section 3.4. It may be pointed out here that the frequencies ν in the relative transition intensity relations (52) and (45b) are not taken into account in our calculation, because it varies very slowly from one line position to another. Also we have used the following in the calculations.

$$\langle \mu_x \rangle = \langle \mu_z \rangle = 1$$

$$T = 293^{\circ}\ K$$

$$\left(\frac{hc}{k}\right) = 1.438786\ ^{\circ}K\text{-cm.}\ \text{(Taken from [4])}$$

Thus, the resulting line strengths and relative transition intensities calculated for up to $J = 10$ are obtained. The results so obtained for the relative transition intensities for the $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$ bands in H_2O and D_2O are given in TABLES III.1, III.2, III.3 and III.4 in APPENDIX III.

4. ROTATION-ELECTRONIC INTERACTION THEORY

4.1 THE ROLE OF ROTATION-ELECTRONIC INTERACTION

In our theory presented in this chapter, it is assumed that the ground state rotational energies are governed, to a good approximation, by the rigid rotor theory. Therefore, the rotational energies in the $\tilde{X}^1A_1$ electronic state can be obtained by using the rigid rotor theory described in Chapter 2.

In the excited states, however, the coupling of electronic angular momentum with rotation results in interaction terms, between the various angular momenta, in the Hamiltonian. Creutzberg and Hougen [5] have discussed the case of purely spin angular momenta for an approximately symmetric-top C_{2V} molecule which results in spin-spin and spin-rotation terms. Their treatment is based on a Hamiltonian given by Raynes [20]. The purely orbital case with which we are concerned may be treated in the same way; this results in orbit-orbit and orbit-rotation terms. In general, where both effects are present, spin-orbit terms are also present.

Our primary objective here is to develop a theory capable of interpreting the rotation-electronic spectra involving transitions to the Rydberg "L - complex" states. In such a case, the electron involved in the transition jumps to a loosely bound outer orbital, characterized by a specific value of the orbital angular momentum quantum number ℓ. The analogous

atomic situation thus gives rise to a $(2\ell + 1)$ degenerate electronic state. In the molecular case, however, this degeneracy is removed by the deviation from spherical symmetry of the molecular ion core. The various states within these $(2\ell + 1)$ states also become mixed as a result of rotation-electronic interaction and consequently, may cause perturbations to the energy level pattern and to the intensity distribution within the rotational branches. Traditional method of reducing spectra may, therefore, need to be supplemented with or replaced by the calculations of the type considered here.

The energy level theory, given in this chapter, is based on a Hamiltonian which includes spin as well as orbital effects and thus also includes the spin theory given by Creutzberg and Hougen [5] . The intensity theory, not previously dealt with, is not as general since it is given here only for a π-complex. Nevertheless, modifications for other cases (including spin) should be reasonably straightforward.

4.2 THE ROTATION-ELECTRONIC HAMILTONIAN

We consider an effective Hamiltonian in the form

$$\hat{H}_{eff} = \hat{H}_{rot} + \hat{H}_{oo} + \hat{H}_{ss} + \hat{H}_{so} + \hat{H}_{sR} + \hat{H}_{oR} \qquad (88)$$

The complete Hamiltonian also contains a vibronic contribution which we assume to be a purely diagonal contribution, $E_{vibronic} = E_e + E_{vib}$, where E_e is the

purely electronic energy while E_{vib} is the simple harmonic oscillator vibrational energy. In (88), $\hat{H}_{rot}$ represents the rigid rotor Hamiltonian while $\hat{H}_{OO}$, $\hat{H}_{SS}$, $\hat{H}_{SO}$, $\hat{H}_{SR}$ and $\hat{H}_{OR}$ represent the orbit-orbit, spin-spin, spin-orbit, spin-rotation and orbit-rotation Hamiltonians, respectively.

We now assume that $\hat{H}_{eff}$ may be rewritten as

$$\hat{H}_{eff} = \sum_i C_i \hat{O}_i \qquad (89)$$

where the summation runs over the terms listed in Table 5 (page 70). The coefficients C_i are the constants corresponding to the operators $\hat{O}_i$ and are summarized in TABLE 5. It may be mentioned that the subscripts LL, SS, LS, LR, and SR on the various constants C_i (TABLE 5) refer to the fact that they belong to the orbit-orbit, spin-spin, orbit-spin, orbit-rotation and spin-rotation interaction terms. Note that C_i are in cm^{-1} units and $\hat{O}_i$ are dimensionless.

From TABLE 5, it is obvious that the total angular momentum $\vec{J}$, the orbital angular momentum $\vec{L}$, and the spin angular momentum $\vec{S}$ are each highly non-diagonal. Therefore, we must have a convenient representation of the effective Hamiltonian $\hat{H}_{eff}$ in a form that separates out the diagonal and off-diagonal matrix elements. To obtain such a form, we have introduced the raising and lowering operators for $\hat{J}$, $\hat{L}$ and $\hat{S}$. If $\hat{J}_+$, $\hat{L}_-$ and $\hat{S}_-$ are the lowering operators and

TABLE 5. THE ANGULAR MOMENTUM OPERATORS $\hat{O}_i$ AND THE CORRESPONDING COEFFICIENTS C_i.

Hamiltonian	C_i	$\hat{O}_i$
$\hat{H}_{rot}$	$\left(\frac{A+C}{2}\right)$	$(\hat{J}-\hat{L}-\hat{S})^2$
	$-\left(\frac{A+C}{2}-B\right)$	$(\hat{J}_z-\hat{L}_z-\hat{S}_z)^2$
	$-\left(\frac{A-C}{2}\right)$	$[(\hat{J}_x-\hat{L}_x-\hat{S}_x)^2-(J_y-L_y-\hat{S}_y)^2]$
$\hat{H}_{oo}$	λ_{LL}	$(3\hat{L}_z^2-\hat{L}^2)$
	δ_{LL}	$(\hat{L}_x^2-\hat{L}_y^2)$
$\hat{H}_{ss}$	λ_{ss}	$(3\hat{S}_z^2-\hat{S}^2)$
	δ_{ss}	$(\hat{S}_x^2-\hat{S}_y^2)$
$\hat{H}_{so}$	γ_{LS}	$(\hat{L}\cdot\hat{S})$
	λ_{LS}	$(3\hat{L}_z\hat{S}_z-\hat{L}\cdot\hat{S})$
	δ_{LS}	$(\hat{L}_x\hat{S}_x-\hat{L}_y\hat{S}_y)$
$\hat{H}_{OR}$	γ_{LR}	$[(\hat{J}-\hat{L}-\hat{S})\cdot\hat{L}]$
	λ_{LR}	$[3(\hat{J}_z-\hat{L}_z-\hat{S}_z)\hat{L}_z - (\hat{J}-\hat{L}-\hat{S})\cdot\hat{L}]$
	δ_{LR}	$[(\hat{J}_x-\hat{L}_x-\hat{S}_x)\hat{L}_x - (\hat{J}_y-\hat{L}_y-\hat{S}_y)\hat{L}_y]$
$\hat{H}_{SR}$	γ_{SR}	$[(\hat{J}-\hat{S}-\hat{L})\cdot\hat{S}]$
	λ_{SR}	$[3(\hat{J}_z-\hat{L}_z-\hat{S}_z)\hat{S}_z - (\hat{J}-\hat{L}-\hat{S})\cdot\hat{S}]$
	δ_{SR}	$[(\hat{J}_x-\hat{L}_x-\hat{S}_x)\hat{S}_x - (\hat{J}_y-\hat{L}_y-\hat{S}_y)\hat{S}_y]$

TABLE 6. OPERATORS AND THEIR CORRESPONDING COEFFICIENTS

Operator $\hat{O}_i$	Coefficient C_i
$\hat{J}^2$	$\frac{1}{2}(A+C)$
$\hat{J}_z^2$	$-\left[\left(\frac{A+C}{2}\right)-B\right]$
$\hat{J}_x^2-\hat{J}_y^2=\frac{1}{2}\left(\hat{J}_+^2+\hat{J}_-^2\right)$	$-\frac{1}{2}(A-C)$
$\hat{L}^2$	$\frac{1}{2}(A+C)-\lambda_{LL}-\gamma_{LR}+\lambda_{LR}$
$\hat{L}_z^2$	$-\left[\frac{1}{2}(A+C)-B\right]+3\lambda_{LL}-3\lambda_{LR}$
$\hat{L}_x^2-\hat{L}_y^2=\frac{1}{2}\left(\hat{L}_+^2+\hat{L}_-^2\right)$	$-\frac{1}{2}(A-C)+\delta_{LL}-\delta_{LR}$
$\hat{S}^2$	$\frac{1}{2}(A+C)-\lambda_{SS}-\gamma_{SR}+\lambda_{SR}$
$\hat{S}_z^2$	$-\left[\frac{A+C}{2}-B\right]+3\lambda_{SS}-3\lambda_{SR}$
$\hat{S}_x^2-\hat{S}_y^2=\frac{1}{2}\left(\hat{S}_+^2+\hat{S}_-^2\right)$	$-\left(\frac{A-C}{2}\right)+\delta_{SS}-\delta_{SR}$
$\hat{J}_z\hat{L}_z$	$-2B+\gamma_{LR}+2\lambda_{LR}$
$\hat{J}_x\hat{L}_x+\hat{J}_y\hat{L}_y=\frac{1}{2}\left(\hat{J}_+\hat{L}_-+\hat{J}_-\hat{L}_+\right)$	$-(A+C)+\gamma_{LR}-\lambda_{LR}$
$\hat{J}_x\hat{L}_x-\hat{J}_y\hat{L}_y=\frac{1}{2}\left(\hat{J}_+\hat{L}_++\hat{J}_-\hat{L}_-\right)$	$(A-C)+\delta_{LR}$
$\hat{J}_z\hat{S}_z$	$-2B+\gamma_{SR}+2\lambda_{SR}$
$\hat{J}_x\hat{S}_x+\hat{J}_y\hat{S}_y=\frac{1}{2}\left(\hat{J}_+\hat{S}_-+\hat{J}_-\hat{S}_+\right)$	$-(A+C)+\gamma_{SR}-\lambda_{SR}$
$\hat{J}_x\hat{S}_x-\hat{J}_y\hat{S}_y=\frac{1}{2}\left(\hat{J}_+\hat{S}_++\hat{J}_-\hat{S}_-\right)$	$(A-C)+\delta_{SR}$
$\hat{L}_z\hat{S}_z$	$2B+\gamma_{LS}-\gamma_{LR}-\gamma_{SR}+2\left(\lambda_{LS}-\lambda_{LR}-\lambda_{SR}\right)$
$\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y=\frac{1}{2}\left(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+\right)$	$(A+C)+\gamma_{LS}-\gamma_{LR}-\gamma_{SR}-\left(\lambda_{LS}-\lambda_{LR}-\lambda_{SR}\right)$
$\hat{L}_x\hat{S}_x-\hat{L}_y\hat{S}_y=\frac{1}{2}\left(\hat{L}_+\hat{S}_++\hat{L}_-\hat{S}_-\right)$	$-(A-C)+\delta_{LS}-\delta_{LR}-\delta_{SR}$

$\hat{J}_-$, $\hat{L}_+$, $\hat{S}_+$ are the raising operators defined by

$$\hat{J}_\pm = \hat{J}_x \pm i\hat{J}_y \quad ; \quad \hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \quad ; \quad \hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \qquad (90)$$

then the resulting operators $\hat{O}_i$ and their corresponding coefficients C_i in $\hat{H}_{eff}$ take the form shown in TABLE 6. Note that the commutation relations for the components of $\hat{\mathcal{J}}$, expressed in the molecular frame, involve the anomalous sign of $i \equiv \sqrt{-1}$. (See Van Vleck [21]). As a consequence, $\hat{J}_+$ becomes the lowering rather than the raising operator.

4.3 FORM OF FUNCTIONS AND MATRIX ELEMENTS

Using a method similar to Kopp and Hougen [17] we choose wavefunctions of the form

$$|JK;\Lambda\Sigma\rangle \equiv |JK\rangle|L\Lambda\rangle|S\Sigma\rangle \tag{91}$$

appropriate to Hunds case (a) where all the angular momenta are well-defined. Here the basis functions $|JK;\Lambda\Sigma\rangle$ are simple products of the total angular momentum part $|JK\rangle$, an electronic orbital part $|L\Lambda\rangle$, an electronic spin part $|S\Sigma\rangle$ and a vibrational part $|v\rangle$, not explicitly shown. J, L and S are the quantum numbers associated with the resultant $\hat{J}$, resultant $\hat{L}$ and resultant $\hat{S}$ operators, respectively. The projections K, Λ and Σ along the z-axis of the molecule -fixed frame are considered as signed quantities.

The phases of $|JK\rangle$, $|L\Lambda\rangle$ and $|S\Sigma\rangle$ are chosen so that $|JK\rangle$ and $|L\Lambda\rangle$ transform according to (20) and (62) respectively while $|S\Sigma\rangle$, having the same transformation properties as $|JK\rangle$, follows the following transformations.

$$\hat{C}_{2z}|S\Sigma\rangle = (-1)^{\Sigma}|S\Sigma\rangle \tag{92a}$$

$$\hat{\sigma}_v(xz)|S\Sigma\rangle = (-1)^{S-\Sigma}|S-\Sigma\rangle \tag{92b}$$

$$\hat{\sigma}_v(yz)|S\Sigma\rangle = (-1)^{S}|S-\Sigma\rangle \tag{92c}$$

Then the operators given by (90) and the operators $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$ and $\hat{S}_z$ have the following effects on their wavefunctions:

$$\hat{J}_{\pm}|JK\rangle = (\hat{J}_x \pm i\hat{J}_y)|JK\rangle = \sqrt{J(J+1) - K(K\mp 1)}\,|JK\mp 1\rangle \quad (93a)$$

$$\hat{L}_{\pm}|L\Lambda\rangle = (\hat{L}_x \pm i\hat{L}_y)|L\Lambda\rangle = \sqrt{L(L+1) - \Lambda(\Lambda\pm 1)}\,|L\Lambda\pm 1\rangle \quad (93b)$$

$$\hat{S}_{\pm}|S\Sigma\rangle = (\hat{S}_x \pm i\hat{S}_y)|S\Sigma\rangle = \sqrt{S(S+1) - \Sigma(\Sigma\pm 1)}\,|S\Sigma\pm 1\rangle \quad (93c)$$

$$\hat{J}^2|JK\rangle = J(J+1)|JK\rangle \quad (93d)$$

$$\hat{L}^2|L\Lambda\rangle = L(L+1)|L\Lambda\rangle \quad (93e)$$

$$\hat{S}^2|S\Sigma\rangle = S(S+1)|S\Sigma\rangle \quad (93f)$$

$$\hat{J}_z|JK\rangle = K|JK\rangle \quad (93g)$$

$$\hat{L}_z|L\Lambda\rangle = \Lambda|L\Lambda\rangle \quad (93h)$$

$$\hat{S}_z|S\Sigma\rangle = \Sigma|S\Sigma\rangle \quad (93i)$$

The results (93) are used to yield the matrix elements, obtained by using the basis functions $|JK;\Lambda\Sigma\rangle$. The resulting diagonal and off-diagonal matrix elements so obtained are shown in TABLE 7. For the molecular systems with zero resultant spin (S = 0), the diagonal and off-diagonal matrix elements become very much simplified; in fact, some of the off-diagonal matrix elements reduce to zero. Then for the zero spin case, since δ_{SS}, δ_{LS}, δ_{SR}, γ_{LS}, γ_{SR}, λ_{SS}, λ_{LS}, λ_{SR}, all reduce to zero, the energy matrix elements in TABLE 7 reduce to the form shown in TABLE 8. Thus

these results (TABLE 8) can be used directly to calculate the eigenvalues and eigenvectors for singlet states.

4.4 THE EIGENFUNCTIONS AND ASSIGNMENT OF SYMMETRY SPECIES TO ROTATIONAL ENERGY LEVELS

If Ψ^{τ} is to represent the total wavefunction of a rotation-electronic state of energy E^{τ}, then

$$\Psi^{\tau} = \sum_{K,\Lambda,\Sigma} a^{\tau}_{K,\Lambda,\Sigma} \, |JK;\Lambda\Sigma\rangle$$

$$= \sum_{K,\Lambda,\Sigma} a^{\tau}_{K,\Lambda,\Sigma} \, |JK\rangle |L\Lambda\rangle |S\Sigma\rangle \qquad (94)$$

where $a^{\tau}_{K,\Lambda,\Sigma}$ are the eigenvectors of the basis functions $|JK;\Lambda\Sigma\rangle$, obtained for an energy level by diagonalizing the energy matrix.

TABLE 7 ENERGY MATRIX ELEMENTS

$$\langle K', \Lambda', \Sigma' \mid K, \Lambda, \Sigma \rangle \equiv \langle J\, K'; \Lambda'\Sigma' \mid \hat{H}_{eff} \mid JK; \Lambda\Sigma \rangle$$

DIAGONAL ELEMENTS :

$$\begin{aligned}
\langle K,\Lambda,\Sigma \mid K,\Lambda,\Sigma \rangle &= \tfrac{1}{2}(A+C)[J(J+1)] + \left[\tfrac{A+C}{2} - \lambda_{LL} - \gamma_{LR} + \lambda_{LR}\right][L(L+1)] \\
&+ \left[\tfrac{A+C}{2} - \lambda_{SS} - \gamma_{SR} + \lambda_{SR}\right][S(S+1)] \\
&- \left[\tfrac{A+C}{2} - B\right]K^2 + \left[-\left(\tfrac{A+C}{2} - B\right) + 3\lambda_{LL} - 3\lambda_{LR}\right]\Lambda^2 \\
&+ \left[-\left(\tfrac{A+C}{2} - B\right) + 3\lambda_{SS} - 3\lambda_{SR}\right]\Sigma^2 \\
&+ \left[-2B + \gamma_{LR} + 2\lambda_{LR}\right]K\Lambda + \left[-2B + \gamma_{SR} + 2\lambda_{SR}\right]K\Sigma \\
&+ \left[2B + \gamma_{LS} - \gamma_{LR} - \gamma_{SR} + 2(\lambda_{LS} - \lambda_{LR} - \lambda_{SR})\right]\Lambda\Sigma
\end{aligned}$$

OFF-DIAGONAL ELEMENTS :

$$\langle K\pm 2, \Lambda, \Sigma \mid K,\Lambda,\Sigma \rangle = -\tfrac{1}{4}(A-C)\langle K\pm 2 \mid K\pm 1\rangle\langle K\pm 1 \mid K\rangle$$

$$\langle K\pm 1, \Lambda\pm 1, \Sigma \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[-(A+C) + \gamma_{LR} - \lambda_{LR}\right]\langle K\pm 1 \mid K\rangle\langle \Lambda\pm 1 \mid \Lambda\rangle$$

$$\langle K\pm 1, \Lambda, \Sigma\pm 1 \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[-(A+C) + \gamma_{SR} - \lambda_{SR}\right]\langle K\pm 1 \mid K\rangle\langle \Sigma\pm 1 \mid \Sigma\rangle$$

$$\langle K\pm 1, \Lambda\mp 1, \Sigma \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[(A-C) + \delta_{LR}\right]\langle K\pm 1 \mid K\rangle\langle \Lambda\mp 1 \mid \Lambda\rangle$$

$$\langle K\pm 1, \Lambda, \Sigma\mp 1 \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[(A-C) + \delta_{SR}\right]\langle K\pm 1 \mid K\rangle\langle \Sigma\mp 1 \mid \Sigma\rangle$$

$$\langle K, \Lambda\pm 2, \Sigma \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[-\tfrac{1}{2}(A-C) + \delta_{LL} - \delta_{LR}\right]\langle \Lambda\pm 2 \mid \Lambda\pm 1\rangle\langle \Lambda\pm 1 \mid \Lambda\rangle$$

$$\langle K, \Lambda, \Sigma\pm 2 \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[-\tfrac{1}{2}(A-C) + \delta_{SS} - \delta_{SR}\right]\langle \Sigma\pm 2 \mid \Sigma\pm 1\rangle\langle \Sigma\pm 1 \mid \Sigma\rangle$$

$$\langle K, \Lambda\pm 1, \Sigma\pm 1 \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[-(A-C) + \delta_{LS} - \delta_{LR} - \delta_{SR}\right]\langle \Lambda\pm 1 \mid \Lambda\rangle\langle \Sigma\pm 1 \mid \Sigma\rangle$$

$$\langle K, \Lambda\pm 1, \Sigma\mp 1 \mid K,\Lambda,\Sigma \rangle = \tfrac{1}{2}\left[(A+C) + \gamma_{LS} - \gamma_{LR} - \gamma_{SR} - (\lambda_{LS} - \lambda_{LR} - \lambda_{SR})\right] \cdot \cdot \langle \Lambda\pm 1 \mid \Lambda\rangle\langle \Sigma\mp 1 \mid \Sigma\rangle$$

Note that for short-hand notation we have defined the following in TABLE 7.

$$\langle K' \mid K\rangle \equiv \sqrt{J(J+1) - KK'}$$

$$\langle \Lambda' \mid \Lambda\rangle \equiv \sqrt{L(L+1) - \Lambda\Lambda'}$$

$$\langle \Sigma' \mid \Sigma\rangle \equiv \sqrt{S(S+1) - \Sigma\Sigma'}$$

TABLE 8 ENERGY MATRIX ELEMENTS (SPIN = 0)

$$\langle K', \Lambda', \Sigma' | K, \Lambda, \Sigma \rangle \equiv \langle JK'; \Lambda'\Sigma' | \hat{H}_{eff} | JK; \Lambda\Sigma \rangle$$

Diagonal Elements:

$$\begin{aligned}\langle K, \Lambda, \Sigma | K, \Lambda, \Sigma \rangle = & \frac{1}{2}(A+C)[J(J+1)] \\ & + \left[\frac{A+C}{2} - \lambda_{LL} - \gamma_{LR} + \lambda_{LR}\right][L(L+1)] \\ & - \left[\frac{A+C}{2} - B\right]K^2 - \left[\left(\frac{A+C}{2} - B\right) - 3\lambda_{LL} + 3\lambda_{LR}\right]\Lambda^2 \\ & + \left[-2B + \gamma_{LR} + 2\lambda_{LR}\right]K\Lambda\end{aligned}$$

Off-Diagonal Elements:

$$\langle K\pm2, \Lambda, \Sigma | K, \Lambda, \Sigma \rangle = -\frac{1}{4}(A-C)\langle K\pm2 | K\pm1\rangle\langle K\pm1 | K\rangle$$

$$\langle K\pm1, \Lambda\pm1, \Sigma | K, \Lambda, \Sigma \rangle = \frac{1}{2}\left[-(A+C) + \gamma_{LR} - \lambda_{LR}\right]\langle K\pm1 | K\rangle\langle\Lambda\pm1 | \Lambda\rangle$$

$$\langle K\pm1, \Lambda\mp1, \Sigma | K, \Lambda, \Sigma \rangle = \frac{1}{2}\left[(A-C) + \delta_{LR}\right]\langle K\pm1 | K\rangle\langle\Lambda\mp1 | \Lambda\rangle$$

$$\langle K, \Lambda\pm2, \Sigma | K, \Lambda, \Sigma \rangle = \frac{1}{2}\left[-\frac{1}{2}(A-C) + \delta_{LL} - \delta_{LR}\right]\langle\Lambda\pm2 | \Lambda\pm1\rangle\langle\Lambda\pm1 | \Lambda\rangle$$

NOTE THAT

$$\langle K' | K\rangle = \sqrt{J(J+1) - KK'}$$

$$\langle\Lambda' | \Lambda\rangle = \sqrt{L(L+1) - \Lambda\Lambda'}$$

$$\langle\Sigma' | \Sigma\rangle = \sqrt{S(S+1) - \Sigma\Sigma'}$$

In view of the transformation properties of $|JK\rangle$, $|L\Lambda\rangle$ and $|S\Sigma\rangle$ for the point group C_{2V}, as is evident from (20a), (62a) and (92a), we find that

$$\hat{C}_{2z}\Psi^{\tau} = \sum_{K,\Lambda,\Sigma} a^{\tau}_{K,\Lambda,\Sigma} (-1)^{K+\Omega} |JK;\Lambda\Sigma\rangle \qquad (95)$$

where $\Omega \equiv \Lambda + \Sigma$ is the total electronic projection along the z-axis of the molecule. (95) shows that under a two-fold rotation of the molecule about the z-axis, Ψ^{τ} will be invariant if $K + \Omega$ is even; otherwise the wavefunction will change to $-\Psi^{\tau}$. That is,

$$\hat{C}_{2z}\Psi^{\tau} = \Psi^{\tau} \text{ for EVEN } (K+\Omega)\text{-VALUES} \qquad (96a)$$

$$\hat{C}_{2z}\Psi^{\tau} = -\Psi^{\tau} \text{ for ODD } (K+\Omega)\text{-VALUES} \qquad (96b)$$

which implies (from character table in APPENDIX I) that

IF $(K+\Omega)$ is EVEN ; Ψ^{τ} is of species A_1 or A_2 (97a)

IF $(K+\Omega)$ is ODD ; Ψ^{τ} is of species B_1 or B_2 (97b)

In order to further find out the conditions which could establish exactly the symmetry of Ψ^{τ} in (97a) and (97b), we consider another symmetry-element of the point group to which the molecule belongs. We consider the reflection plane $\hat{\sigma}_v(yz)$, which is another

element of the point group C_{2V}. Then from (20b), (62c) and (92c), one finds that

$$\hat{\sigma}_v(yz)\,|\,J K;\Lambda\Sigma\rangle = (-1)^{J+S}\,|\,J-K\rangle\,|\,L-\Lambda\rangle\,|\,S-\Sigma\rangle \qquad (98)$$

Then,

$$\hat{\sigma}_v(yz)\,\Psi^{\tau} = (-1)^{J+S}\sum_{K,\Lambda,\Sigma} a^{\tau}_{K,\Lambda,\Sigma}\,|\,J-K\,;-\Lambda-\Sigma\rangle \qquad (99a)$$

Here we have two possibilities. Either (99a) is $+\Psi^{\tau}$ or $-\Psi^{\tau}$. That is,

$$\hat{\sigma}_v(yz)\Psi^{\tau} = \pm\sum_{K,\Lambda,\Sigma} a^{\tau}_{K,\Lambda,\Sigma}\,|\,J K;\Lambda\Sigma\rangle \equiv \pm\,\Psi^{\tau} \qquad (99b)$$

In order to satisfy this condition, let us first suppose that

$$a^{\tau}_{K,\Lambda,\Sigma} = a^{\tau}_{-K,-\Lambda,-\Sigma} \qquad (99c)$$

then (99a) becomes

$$\hat{\sigma}_v(yz)\Psi^{\tau} = (-1)^{J+S}\sum_{K,\Lambda,\Sigma} a^{\tau}_{-K,-\Lambda,-\Sigma}\,|\,J-K;-\Lambda-\Sigma\rangle \qquad (99d)$$

$$= (-1)^{J+S}\Psi^{\tau}$$

Similarly, if

$$a^{\tau}_{K,\Lambda,\Sigma} = -\,a^{\tau}_{-K,\Lambda,-\Sigma} \qquad (99e)$$

then,

$$\hat{\sigma}_v(yz)\Psi^{\tau} = -(-1)^{J+S}\Psi^{\tau} \qquad (99f)$$

Thus, the results given by (99) lead to the conclusion that

$$\hat{\sigma}_v(yz)\Psi^\tau = \pm(-1)^{J+S}\Psi^\tau \quad \text{if} \quad a^\tau_{K,\Lambda,\Sigma} = \pm a^\tau_{-K,-\Lambda,-\Sigma} \tag{99g}$$

Now from (99g) and the character table (APPENDIX I), we find that

$$\hat{\sigma}_v(yz)\Psi^\tau = \begin{cases} +\Psi^\tau & \text{refers to species } A_1 \text{ or } B_1 \\ -\Psi^\tau & \text{refers to species } A_2 \text{ or } B_1 \end{cases} \tag{99h}$$

Thus, the results (96), (97) and (99g), (99h) establish the criteria for assigning the symmetry species to each rotational energy states. The criteria is summarized in TABLE 9. Note that a complete symmetry of an electronic state is obtained by multiplying the above established symmetry with that of the core. Also, for singlet states (S = 0), we can readily get exactly the same criteria by merely replacing $J + S$ and $K + \Omega$ in TABLE 9 by J and $K + \Lambda$, respectively. Similarly, the replacements (in TABLE 9) of $J + S$ by J and $K + \Omega$ by K gives the criteria for purely rotational states. The resulting conditions for the symmetry of rotational states are the same as those already given in TABLE 1 (Chapter 2).

TABLE 9 CRITERIA FOR ASSIGNING THE FULL MOLECULAR SPECIES TO THE ROTATION-ELECTRONIC STATES FOR THE MOLECULES OF SYMMETRY C_{2V}

$J+S$	$K+\Omega$	$a^{\tau}_{K,\Lambda,\Sigma} = a^{\tau}_{-K,-\Lambda,-\Sigma}$ Symmetry Species	$a^{\tau}_{K,\Lambda,\Sigma} = -a^{\tau}_{-K,-\Lambda,-\Sigma}$ Symmetry Species
EVEN	EVEN	A_1	A_2
EVEN	ODD	B_2	B_1
ODD	EVEN	A_2	A_1
ODD	ODD	B_1	B_2

4.5 THE THEORY OF RELATIVE TRANSITION INTENSITIES

In this section, expressions for the line strengths and the corresponding relative intensities are obtained for rotation-electronic dipole transitions. Electric dipole transitions are governed by the matrix elements

$$\langle f | \mu_Z | i \rangle \tag{100}$$

where $|i\rangle$ and $\langle f|$ are respectively the initial and final rovibronic states between which transitions take place. μ_Z, having symmetry species A_2, is the space-fixed Z-component of the dipole moment $\vec{\mu}$. In order to be non-zero, the integral (100) must be totally symmetric. Then,

$$\Gamma(f) \times \Gamma(i) = A_2 \tag{101}$$

where $\Gamma(i)$ and $\Gamma(f)$ are the irreducible representations of the initial and final states $|i\rangle$ and $\langle f|$ respectively.

Let us now write

$$|i\rangle = \psi''_{evr} = \psi''_{ev}\,\psi''_{r} \tag{102a}$$

where ψ''_{ev} is the complete vibronic part and ψ''_{r} is the rotational part. The electronic portion of the final state must be separated into a core, which may be included with the vibrational part, and a single electron state which must be combined with the rotational part. That is,

$$|f\rangle \equiv \psi'_{evr} = \psi'_{CORE,\,v} \cdot \psi'_{er} \tag{102b}$$

Assuming ψ''_{ev} and ψ'_{v} to be totally symmetric we thus see that (101) may be rewritten as

$$[\Gamma'_{CORE} \times \Gamma'_{er}] \times \Gamma''_{r} = A_2 \tag{103}$$

or

$$\Gamma'_{er} \times \Gamma''_{r} = A_2 \times \Gamma'_{CORE} \tag{104}$$

Note that Γ''_{r} and Γ'_{er} represent the initial and final states' "rotational" symmetries given by our previously discussed rules. The complete state symmetries are given by Γ''_{r} and $\Gamma'_{CORE} \times \Gamma'_{er}$ for the initial and final states respectively.

Now with the choice of rotation-electronic wavefunctions given by (94), consistent with our assumption for vibrational states, let $\Psi^{\tau''}$ and $\Psi^{\tau'}$ be the wavefunctions of the initial and final states of energies $E^{\tau''}$ and $E^{\tau'}$ respectively, between which transitions are considered, then the dipole transition moments are given by

$$\langle \Psi^{\tau'} | \mu_Z | \Psi^{\tau''} \rangle = \sum_{\substack{K'', \Lambda'', \Sigma'', \\ K', \Lambda', \Sigma'}} a^{\tau''}_{K'', \Lambda'', \Sigma''} \, a^{\tau'}_{K', \Lambda', \Sigma'} \langle J'K'; \Lambda'\Sigma' | \sum_r f_{-r} \mu_r | J''K''; \Lambda''\Sigma'' \rangle \tag{105}$$

where μ_Z is the space-fixed Z -component of dipole moment $\vec{\mu}$; f_{-r} are appropriate functions of the direction cosines and μ_r represents the components of a spherical tensor of rank unity (see (35) in Chapter 2). The expression given by the right hand side of (105) is general in the sense that it includes both the orbital and the electronic spin. Then the line strength $[S]^{J''}_{J'}$ is given by the spatial average (see Lepard [13]):

$$[S]^{J''}_{J'} = \overline{|\langle \Psi^{\tau'}(J') | \mu_Z | \Psi^{\tau''}(J'') \rangle|^2} = \frac{1}{3}[G]^{J''}_{J'} \qquad (106)$$

where

$$[G]^{J''}_{J'} = \Big| \sum_{\substack{K'',\Lambda'',\Sigma'',\\ K',\Lambda',\Sigma'}} a^{\tau''}_{K'',\Lambda'',\Sigma''}\, a^{\tau'}_{K',\Lambda',\Sigma'} \langle J'K';\Lambda'\Sigma' | \sum_r f_{-r}\mu_r | J''K'';\Lambda''\Sigma'' \rangle \Big|^2 \qquad (107)$$

where $|J''K'';\Lambda''\Sigma''\rangle$ and $|J'K';\Lambda'\Sigma'\rangle$ are the rotation-electronic basis functions for the initial and final states of combination. Then in view of (91) we can write

$$[G]^{J''}_{J'} = \Big| \sum_{\substack{K'',\Lambda'',\Sigma'',\\ K',\Lambda',\Sigma',r}} a^{\tau''}_{K'',\Lambda'',\Sigma''}\, a^{\tau'}_{K',\Lambda',\Sigma'} \langle \Lambda'\Sigma' | \mu_r | \Lambda''\Sigma'' \rangle \langle J'K' | f_{-r} | J''K'' \rangle \Big|^2 \qquad (108)$$

where $\Delta J = J' - J'' = 0, \pm 1$ and $r = \Delta K = K' - K'' = 0, \pm 1$.

Since $\vec{\mu}$ is an orbital function, the electronic integral has a value only when $\Delta S = \Delta\Sigma = 0$. Then from (108), we may rewrite (106) in the form

$$[S]^{J''}_{J'} = \frac{1}{3}\left| \sum_{\substack{K'',\Lambda'',\Sigma'',\\ K',\Lambda',\Delta K}} a^{\tau''}_{K'',\Lambda'',\Sigma''}\, a^{\tau'}_{K',\Lambda',\Sigma''} \langle \Lambda'\Sigma'' | \mu_{\Delta K} | \Lambda''\Sigma'' \rangle \langle J'K' | f_{-\Delta K} | J''K'' \rangle \right|^2 \tag{109}$$

The corresponding expression for the relative intensities for the dipole transitions can be written as

$$[I]^{J''}_{J'} = \nu g_{J''} (2J''+1) e^{-E/T^*} [S]^{J''}_{J'} \tag{110}$$

where

ν = Frequency of absorption.

$g_{J''}$ = Nuclear statistical weight for the initial state.

E = Energy of the lower state in cm^{-1}.

$T^* = T/\left(\frac{hc}{k}\right) = T/$(Second Radiation Constant)

T = Temperature in absolute units (^oK).

For the transitions involving singlet states only, (109) and (110) reduce to

$$[S]^{J''}_{J'} = \frac{1}{3}\left| \sum_{\substack{K'',\Lambda'',\\ K',\Lambda',\Delta K}} a^{\tau''}_{K'',\Lambda''}\, a^{\tau'}_{K',\Lambda'} \langle \Lambda' | \mu_{\Delta K} | \Lambda'' \rangle \langle J'K' | f_{-\Delta K} | J''K'' \rangle \right|^2 \tag{111}$$

and

$$[I]^{J''}_{J'} = \nu g_{J''} (2J''+1) e^{-E/T^*} [S]^{J''}_{J'} \qquad (112)$$

The non-vanishing rotational matrix elements are given in TABLE 2 (Chapter 2) while the non-vanishing electronic matrix elements are determined by requiring the elements $\langle \Lambda' | \mu_{\Delta K} | \Lambda'' \rangle$ to be totally symmetric.

4.6 RELATIVE INTENSITIES FOR THE SINGLET-SINGLET TRANSITIONS TO $3p$-COMPLEX

The transitions between the ground state and the excited electronic states corresponding to $L = 1$ are governed by (111) and (112) where $\Lambda = 0, \pm 1$. Since the overall symmetry of the ground electronic state is taken as totally symmetric, then $|\Lambda''\rangle \equiv |\Lambda_G\rangle = |A_1\rangle$ for the ground rovibronic state. $|\Lambda_G\rangle$ indicates the ground electronic state. Then (111) reduces to

$$[S]^{J''}_{J'} = \frac{1}{3} \left| \sum_{K'', K', \Delta K} a^{\tau''}_{K''} \langle J'K' | f_{-\Delta K} | J''K'' \rangle \left[a^{\tau'}_{K',-1} \langle -1 | \mu_{\Delta K} | A_1 \rangle + a^{\tau'}_{K',0} \langle 0 | \mu_{\Delta K} | A_1 \rangle + a^{\tau'}_{K',1} \langle 1 | \mu_{\Delta K} | A_1 \rangle \right] \right|^2 \qquad (113)$$

The symmetry conditions for non-zero integrals $\langle \Lambda' | \mu_{\Delta K} | \Lambda \rangle$ are examined below. We must use the complete symmetry of the levels and thus the Γ'_{er} of the upper state must be multiplied by Γ'_{core}.

CASE (I): B_1 MOLECULAR CORE

We use the symmetry elements $\hat{\sigma}_v(xz)$ and $\hat{\sigma}_v(yz)$. The components of dipole moment transform as follows:

$$\hat{\sigma}_v(xz)\mu_\pm = \mu_\mp \tag{114a}$$

$$\hat{\sigma}_v(yz)\mu_o = \mu_o \tag{114b}$$

$$\hat{\sigma}_v(xz)\mu_\pm = -\mu_\mp \tag{115a}$$

$$\hat{\sigma}_v(yz)\mu_o = \mu_o \tag{115b}$$

The upper state (i.e. the excited state) electronic functions, including the B_1 molecular core, transform as

$$\hat{\sigma}_v(xz)|\Lambda\rangle = (-1)^\Lambda|-\Lambda\rangle \tag{116}$$

$$\hat{\sigma}_v(yz)|\Lambda\rangle = -|-\Lambda\rangle \tag{117}$$

where, for the sake of brevity, the electronic functions are defined by $|L\Lambda\rangle \equiv |\Lambda\rangle$. Then from (114), (115), (116) and (117) one finds that

$$\hat{\sigma}_v(xz)\langle -1|\mu_o|A_1\rangle = -\langle 1|\mu_o|A_1\rangle \tag{118a}$$

$$\hat{\sigma}_v(yz)\langle -1|\mu_o|A_1\rangle = -\langle 1|\mu_o|A_1\rangle \tag{118b}$$

$$\hat{\sigma}_v(xz)\langle 0|\mu_o|A_1\rangle = \langle 0|\mu_o|A_1\rangle \tag{119a}$$

$$\hat{\sigma}_v(yz)\langle 0|\mu_o|A_1\rangle = -\langle 0|\mu_o|A_1\rangle \tag{119b}$$

$$\hat{\sigma}_v(xz)\langle 1|\mu_o|A_1\rangle = -\langle -1|\mu_o|A_1\rangle \tag{120a}$$

$$\hat{\sigma}_v(yz)\langle 1|\mu_o|A_1\rangle = -\langle -1|\mu_o|A_1\rangle \tag{120b}$$

$$\hat{\sigma}_v(xz)\langle -1|\mu_\pm|A_1\rangle = -\langle 1|\mu_\mp|A_1\rangle \tag{121a}$$

$$\hat{\sigma}_v(yz)\langle -1|\mu_\pm|A_1\rangle = \langle 1|\mu_\mp|A_1\rangle \tag{121b}$$

$$\hat{\sigma}_v(xz)\langle 0|\mu_\pm|A_1\rangle = \langle 0|\mu_\mp|A_1\rangle \qquad (122a)$$

$$\hat{\sigma}_v(yz)\langle 0|\mu_\pm|A_1\rangle = \langle 0|\mu_\mp|A_1\rangle \qquad (122b)$$

$$\hat{\sigma}_v(xz)\langle 1|\mu_\pm|A_1\rangle = -\langle -1|\mu_\mp|A_1\rangle \qquad (123a)$$

$$\hat{\sigma}_v(yz)\langle 1|\mu_\pm|A_1\rangle = \langle -1|\mu_\mp|A_1\rangle \qquad (123b)$$

Since the effect of $\hat{\sigma}_v(xz)$ and $\hat{\sigma}_v(yz)$ on $\langle -1|\mu_0|A_1\rangle$ is the same in (118a) and (118b), each of (118a) and (118b) must be equal to the operand $\langle -1|\mu_0|A_1\rangle$ in order that this matrix element be non-zero. Note that the use of the $\hat{C}_{2z}$ operator or the identity operator does not add any new information and, therefore, their use will be redundant. Only two of the four molecular point group elements are sufficient here.

We conclude, therefore, that

$$\langle -1|\mu_0|A_1\rangle = -\langle 1|\mu_0|A_1\rangle \neq 0 \qquad (124a)$$

(120a) and (120b) together also lead to the same result (124a). Similarly, to be non-vanishing, (119a) and (119b) each must be equal to $\langle 0|\mu_0|A_1\rangle$. But here the effect of $\hat{\sigma}_v(xz)$ and $\hat{\sigma}_v(yz)$ on $\langle 0|\mu_0|A_1\rangle$ give opposite signs to the same resulting quantity. This implies that

$$\langle 0|\mu_0|A_1\rangle = 0 \qquad (124b)$$

In a similar fashion, for the equations (121a), (121b), (122a), (122b) and (123a), (123b) we conclude

that

$$\langle -1 | \mu_{\pm} | A_1 \rangle = \langle 1 | \mu_{\mp} | A_1 \rangle = 0 \qquad (124c)$$

$$\langle 0 | \mu_{+} | A_1 \rangle = \langle 0 | \mu_{-} | A_1 \rangle \neq 0 \qquad (124d)$$

where (124c) is obtained independently by the pairs of equations (121a), (121b) and (123a), (123b). Thus we have established that on the basis of symmetry requirements some of the matrix elements do reduce to zero.

Now, our next step is to see if the non-zero matrix elements are real or imaginary. For this purpose a time reversal operator $\hat{\theta}_t$ is introduced here which, by giving the complex conjugate of the operand, decides whether a quantity (i.e., an operand) is real or imaginary depending upon whether the quantity under consideration remains invariant or changes sign.

We assume a choice of phase so that the lower state and also the upper state core are each represented by real functions. then, from spherical harmonics we see that orbital functions obey

$$\hat{\theta}_t | \Lambda \rangle = (-1)^{\Lambda} | -\Lambda \rangle \qquad (125)$$

Therefore, from (125) and (124a), one obtains

$$\hat{\theta}_t \langle -1 | \mu_0 | A_1 \rangle = - \langle 1 | \mu_0 | A_1 \rangle = \langle -1 | \mu_0 | A_1 \rangle \qquad (126)$$

which implies that $\langle -1|\mu_0|A_1\rangle$ is real. That is,

$$\langle -1|\mu_0|A_1\rangle = -\langle 1|\mu_0|A_1\rangle = \text{REAL}. \tag{127}$$

Again from (125) and (124d), one obtains

$$\hat{\theta}_t\langle 0|\mu_+|A_1\rangle = \langle 0|\mu_-|A_1\rangle = \langle 0|\mu_+|A_1\rangle \tag{128}$$

which implies that

$$\langle 0|\mu_+|A_1\rangle = \langle 0|\mu_-|A_1\rangle = \text{REAL} \tag{129}$$

Thus we summarize our conclusions as follows

$$\left.\begin{aligned}
&\langle -1|\mu_0|A_1\rangle = -\langle 1|\mu_0|A_1\rangle = \text{REAL} \neq 0\\
&\langle -1|\mu_\pm|A_1\rangle = \langle 1|\mu_\mp|A_1\rangle = 0\\
&\langle 0|\mu_0|A_1\rangle = 0\\
&\langle 0|\mu_+|A_1\rangle = \langle 0|\mu_-|A_1\rangle = \text{REAL} \neq 0
\end{aligned}\right\} \tag{130}$$

In view of the results (130), the expression for the line strengths of spectral absorption lines, (113), becomes

$$\begin{aligned}
[S]^{J''}_{J'} = \frac{1}{3}\Bigg| \sum_{K''} a^{\tau''}_{K''} \Big\{ & a^{\tau'}_{K'',-1}\langle J'K''|f_0|J''K''\rangle\langle -1|\mu_0|A_1\rangle\\
& + a^{\tau'}_{K''+1,0}\langle J'K''+1|f_-|J''K''\rangle\langle 0|\mu_+|A_1\rangle\\
& + a^{\tau'}_{K''-1,0}\langle J'K''-1|f_+|J''K''\rangle\langle 0|\mu_-|A_1\rangle\\
& + a^{\tau'}_{K'',1}\langle J'K''|f_0|J''K''\rangle\langle 1|\mu_0|A_1\rangle\Big\}\Bigg|^2
\end{aligned} \tag{131}$$

Now (131) can be reduced further so that one can determine the components of $\vec{\mu}$, in the molecule-fixed frame, which are active in each matrix element. Consequently, the selection rules for transitions can be set forth in terms of the symmetry species of electronic energy states.

It is useful to note that the electronic integrals in (131) may be expressed in terms of purely electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$ defined by (58). These relations may be combined with those given for $\mu_\pm$ and μ_0 by (34) to yield

$$\langle 0|\mu_0|A_1\rangle = \langle z|\mu_z|A_1\rangle \tag{132a}$$

$$\langle 0|\mu_\pm|A_1\rangle = \frac{1}{\sqrt{2}}\langle z|\mu_x|A_1\rangle \pm \frac{i}{\sqrt{2}}\langle z|\mu_y|A_1\rangle \tag{132b}$$

$$\langle \pm 1|\mu_0|A_1\rangle = \frac{1}{\sqrt{2}}\langle y|\mu_z|A_1\rangle \pm \frac{1}{\sqrt{2}}\langle x|\mu_z|A_1\rangle \tag{132c}$$

$$\langle 1|\mu_\pm|A_1\rangle = \frac{1}{2}\langle y|\mu_x|A_1\rangle + \frac{1}{2}\langle x|\mu_x|A_1\rangle \pm \frac{i}{2}\langle y|\mu_y|A_1\rangle \pm \frac{i}{2}\langle x|\mu_y|A_1\rangle \tag{132d}$$

$$\langle -1|\mu_\pm|A_1\rangle = \frac{1}{2}\langle y|\mu_x|A_1\rangle - \frac{1}{2}\langle x|\mu_x|A_1\rangle \pm \frac{i}{2}\langle y|\mu_y|A_1\rangle \mp \frac{i}{2}\langle x|\mu_y|A_1\rangle \tag{132e}$$

The states $|x\rangle$, $|y\rangle$ and $|z\rangle$ are of symmetry species A_1, A_2 and B_1 respectively, for a core of symmetry

species B_1. Since μ_x, μ_y, μ_z are of symmetry B_1 B_2, A_1, respectively, the right hand side of the above equations reduces to one non-zero totally symmetric term. These may be written, using (130), as follows:

$$\langle 0|\mu_\pm|A_1\rangle = \frac{1}{\sqrt{2}}\langle z|\mu_x|A_1\rangle \equiv \frac{1}{\sqrt{2}}\langle\mu_x\rangle \tag{133a}$$

$$\pm\langle\pm 1|\mu_0|A_1\rangle = \frac{1}{\sqrt{2}}\langle x|\mu_z|A_1\rangle \equiv \frac{1}{\sqrt{2}}\langle\mu_z\rangle \tag{133b}$$

where $\langle\mu_x\rangle$ and $\langle\mu_z\rangle$ are real.

Then by making use of the results (133) in (131), we obtain

$$[S]^{J''}_{J'} = \frac{1}{6}\left|\sum_{K''} a^{\tau''}_{K''}\left[\left(a^{\tau'}_{K''-1,0}\langle J'K''-1|f_+|J''K''\rangle + a^{\tau'}_{K''+1,0}\langle J'K''+1|f_-|J''K''\rangle\right)\langle\mu_x\rangle + \left(a^{\tau'}_{K'',1} - a^{\tau'}_{K'',-1}\right)\langle J'K''|f_0|J''K''\rangle\langle\mu_z\rangle\right]\right|^2 \tag{134}$$

Note that the existence of $\langle\mu_x\rangle$ and $\langle\mu_z\rangle$ implies, ignoring rotation, purely electronic transitions to states $\tilde{D}\,^1A_1$ and $\tilde{C}\,^1B_1$. However, unlike the previous treatment (Chapter 2), both $\langle\mu_x\rangle$ and $\langle\mu_z\rangle$ participate in the transition to each state, as is evident from (134).

In order to investigate the effect of both moments participating in a given transition, we shall consider the following limiting cases:

CASE	$\langle \mu_z \rangle$	$\langle \mu_x \rangle$
(a)	1	0
(b)	0	1
(c)	1	1
(d)	1	-1

The actual case, to be determined by examination of the experimental spectra, should lie within the above cases. Then for the case (a), only μ_z terms will be non-zero while for the case (b), μ_x terms will be non-zero. In cases (c) and (d), both the terms will exist in (134) and, therefore, there will be a mixture of transitions involving μ_x and μ_z both. Thus for:

CASE I (a):

$$[S]^{J''}_{J'} = \frac{1}{6}\left| \sum_{K''} a^{\tau''}_{K''} \left(a^{\tau'}_{K'',1} - a^{\tau'}_{K'',-1}\right) \langle J'K'' | f_o | J''K'' \rangle \right|^2 \qquad (135a)$$

CASE I (b):

$$[S]^{J''}_{J'} = \frac{1}{6}\left| \sum_{K''} a^{\tau''}_{K''} \left(a^{\tau'}_{K''-1,o} \langle J'K''-1 | f_+ | J''K'' \rangle + a^{\tau'}_{K''+1,o} \langle J'K''+1 | f_- | J''K'' \rangle\right) \right|^2 \qquad (135b)$$

CASE I (c):

$$[S]^{J''}_{J'} = \frac{1}{6}\left| \sum_{K''} a^{\tau''}_{K''} \left[\left(a^{\tau'}_{K''-1,o} \langle J'K''-1 | f_+ | J''K'' \rangle + a^{\tau'}_{K''+1,o} \langle J'K''+1 | f_- | J''K'' \rangle\right) + \left(a^{\tau'}_{K'',1} - a^{\tau'}_{K'',-1}\right) \langle J'K'' | f_o | J''K'' \rangle \right] \right|^2 \qquad (135c)$$

CASE I (d):

$$[S]^{J''}_{J'} = \frac{1}{6}\left| \sum_{K''} a^{\tau''}_{K''} \left[-\left(a^{\tau'}_{K''-1,o} \langle J'K''-1 | f_+ | J''K'' \rangle + a^{\tau'}_{K''+1,o} \langle J'K''+1 | f_- | J''K'' \rangle\right) + \left(a^{\tau'}_{K'',1} - a^{\tau'}_{K'',-1}\right) \langle J'K'' | f_o | J''K'' \rangle \right] \right|^2 \qquad (135d)$$

CASE (II): B_2 MOLECULAR CORE

In the case where a molecular core symmetry B_2 is involved, we adopt exactly a similar procedure as for the molecular core B_1 (CASE (1)). However, since the ground state is assumed to have the symmetry A_1 as before, the transformations of $|\Lambda\rangle$, with the molecular core B_2 included, will be

$$\hat{\sigma}_v(xz)|\Lambda\rangle = -(-1)^{\Lambda}|-\Lambda\rangle \tag{136a}$$

$$\hat{\sigma}_v(yz)|\Lambda\rangle = |-\Lambda\rangle \tag{136b}$$

which, together with the use of time reversal operator $\hat{\theta}_t$, give the results

$$\left.\begin{aligned} &\langle -1|\mu_0|A_1\rangle = \langle 1|\mu_0|A_1\rangle = \text{IMAGINARY} \neq 0 \\ &\langle 0|\mu_0|A_1\rangle = 0 \\ &\langle -1|\mu_\pm|A_1\rangle = \langle 1|\mu_\mp|A_1\rangle = 0 \\ &\langle 0|\mu_+|A_1\rangle = -\langle 0|\mu_-|A_1\rangle = \text{IMAGINARY} \neq 0 \end{aligned}\right\} \tag{137}$$

The symmetry species of the electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$, with the molecular core B_2 included, become A_2, A_1 and B_2, respectively. The (137) may be written, when reducing (132) as before, as follows:

$$\pm\langle 0|\mu_\pm|A_1\rangle = \frac{i}{\sqrt{2}}\langle z|\mu_y|A_1\rangle \equiv \frac{1}{\sqrt{2}}\langle \mu_y\rangle \tag{138a}$$

$$\langle \pm 1|\mu_0|A_1\rangle = \frac{1}{\sqrt{2}}\langle y|\mu_z|A_1\rangle \equiv \frac{1}{\sqrt{2}}\langle \mu_z\rangle \tag{138b}$$

where $\langle \mu_y \rangle$ and $\langle \mu_z \rangle$ are purely imaginary. Then, the expression for the line strength, from (113), (137) and (138) becomes

$$[S]^{J''}_{J'} = \frac{1}{6} \Big| \sum_{K''} a^{\tau''}_{K''} \Big[\big(a^{\tau'}_{K''+1,0} \langle J'K''+1 | f_- | J''K'' \rangle - a^{\tau'}_{K''-1,0} \langle J'K''-1 | f_+ | J''K'' \rangle \big) \langle \mu_y \rangle + \big(a^{\tau'}_{K'',-1} + a^{\tau'}_{K'',1} \big) \langle J'K'' | f_0 | J''K'' \rangle \langle \mu_z \rangle \Big] \Big|^2 \tag{139}$$

Since both $\langle \mu_y \rangle$ and $\langle \mu_z \rangle$ are imaginary, we may simply use, instead, real numbers in the formula (139).

CASE (III): A_1 MOLECULAR CORE

In this case, with the core A_1 included, we have

$$\hat{\sigma}_v(xz) |\Lambda\rangle = (-1)^{\Lambda} |-\Lambda\rangle \tag{140a}$$

$$\hat{\sigma}_v(yz) |\Lambda\rangle = |-\Lambda\rangle \tag{140b}$$

which when used in combination with the time reversal operator $\hat{\theta}_t$ on the purely electronic matrix elements give the results

$$\left.\begin{aligned} &\langle -1 | \mu_0 | A_1 \rangle = \langle 1 | \mu_0 | A_1 \rangle = 0 \\ &\langle 0 | \mu_0 | A_1 \rangle = \text{REAL} \neq 0 \\ &\langle -1 | \mu_\pm | A_1 \rangle = -\langle 1 | \mu_\mp | A_1 \rangle = \text{REAL} \neq 0 \\ &\langle 0 | \mu_+ | A_1 \rangle = \langle 0 | \mu_- | A_1 \rangle = 0 \end{aligned}\right\} \tag{141}$$

The symmetry species of the electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$, with the molecular core symmetry A_1 included, are B_1, B_2 and A_1, respectively. Then (141) may be written, when reducing (132) as before, as follows:

$$\langle 0|\mu_0|A_1\rangle = \langle z|\mu_z|A_1\rangle \equiv \langle \mu_z\rangle \tag{142a}$$

$$\begin{aligned}\langle 1|\mu_\pm|A_1\rangle &= -\langle -1|\mu_\mp|A_1\rangle \\ &= \tfrac{1}{2}\langle x|\mu_x|A_1\rangle \pm \tfrac{i}{2}\langle y|\mu_y|A_1\rangle \\ &= \tfrac{1}{2}\langle \mu_x\rangle \pm \tfrac{1}{2}\langle \mu_y\rangle\end{aligned} \tag{142b}$$

where $\langle \mu_x\rangle = \langle x|\mu_x|A_1\rangle$ and $\langle \mu_y\rangle = i\langle y|\mu_y|A_1\rangle$ are purely real. Then, the expression for the line strength, from (113), (141) and (142) becomes

$$\begin{aligned}[S]^{J''}_{J'} = \frac{1}{3}\Bigg|\sum_{K''} a^{\tau''}_{K''}\Bigg[&\Big\{\big(a^{\tau'}_{K''-1,1} - a^{\tau'}_{K''-1,-1}\big)\langle J'K''-1|f_+|J''K''\rangle \\ &+\big(a^{\tau'}_{K''+1,1} - a^{\tau'}_{K''+1,-1}\big)\langle J'K''+1|f_-|J''K''\rangle\Big\}\frac{\langle\mu_x\rangle}{2} \\ &+\Big\{-\big(a^{\tau'}_{K''-1,1} + a^{\tau'}_{K''-1,-1}\big)\langle J'K''-1|f_+|J''K''\rangle \\ &+\big(a^{\tau'}_{K''+1,1} + a^{\tau'}_{K''+1,-1}\big)\langle J'K''+1|f_-|J''K''\rangle\Big\}\frac{\langle\mu_y\rangle}{2} \\ &+\Big\{a^{\tau'}_{K'',0}\langle J'K''|f_0|J''K''\rangle\Big\}\langle\mu_z\rangle\Bigg]\Bigg|^2\end{aligned} \tag{143}$$

Here we note that $\langle\mu_x\rangle$, $\langle\mu_y\rangle$ and $\langle\mu_z\rangle$ are all real quantities. Also we note that all the components of participate in the transition for a totally symmetric molecular core.

CASE (IV): A_2 MOLECULAR CORE:

Here, with the core A_2 included, we have

$$\hat{\sigma}_v(xz)|\Lambda\rangle = -(-1)^{\Lambda}|-\Lambda\rangle \tag{144a}$$

$$\hat{\sigma}_v(yz)|\Lambda\rangle = -|-\Lambda\rangle \tag{144b}$$

which, on using the time reversal operator $\hat{\theta}_t$, give the results

$$\left.\begin{aligned} &\langle -1|\mu_0|A_1\rangle = \langle 1|\mu_0|A_1\rangle = 0 \\ &\langle 0|\mu_0|A_1\rangle = 0 \\ &\langle -1|\mu_\pm|A_1\rangle = \langle 1|\mu_\mp|A_1\rangle = \text{IMAGINARY} \neq 0 \\ &\langle 0|\mu_+|A_1\rangle = \langle 0|\mu_-|A_1\rangle = 0 \end{aligned}\right\} \tag{145}$$

We find that the symmetry species of the electronic states $|x\rangle$, $|y\rangle$ and $|z\rangle$, with the molecular core A_2 included, are B_2, B_1 and A_2, respectively. Then (145) may be written, when reducing (132) as before, as follows:

$$\begin{aligned} \langle 1|\mu_\pm|A_1\rangle &= \langle -1|\mu_\mp|A_1\rangle \\ &= \tfrac{1}{2}\langle y|\mu_x|A_1\rangle \pm \tfrac{i}{2}\langle x|\mu_y|A_1\rangle \\ &= \tfrac{1}{2}\langle \mu_x\rangle \pm \tfrac{1}{2}\langle \mu_y\rangle \end{aligned} \tag{146}$$

where $\langle \mu_x\rangle = \langle y|\mu_x|A_1\rangle$ and $\langle \mu_y\rangle = i\langle x|\mu_y|A_1\rangle$ are purely imaginary. Then, from (113), (145) and (146), the expression for the line strength becomes

$$[S]^{J''}_{J'} = \frac{1}{12}\left| \sum_{K''} a^{\tau''}_{K''} \left[\left\{ \left(a^{\tau'}_{K''-1,-1} + a^{\tau'}_{K''-1,1} \right) \langle J'K''-1 | f_+ | J''K'' \rangle \right.\right.\right.$$

$$\left. + \left(a^{\tau'}_{K''+1,-1} + a^{\tau'}_{K''+1,1} \right) \langle J'K''+1 | f_- | J''K'' \rangle \right\} \langle \mu_x \rangle$$

$$+ \left\{ \left(a^{\tau'}_{K''-1,-1} - a^{\tau'}_{K''-1,1} \right) \langle J'K''-1 | f_+ | J''K'' \rangle \right.$$

$$\left.\left.\left. - \left(a^{\tau'}_{K''+1,-1} - a^{\tau'}_{K''+1,1} \right) \langle J'K''+1 | f_- | J''K'' \rangle \right\} \langle \mu_y \rangle \right] \right|^2$$

(147)

Thus, we see that both the moments $\langle \mu_x \rangle$ and $\langle \mu_y \rangle$ participate in the transition when the molecular core A_2 is involved. Also both $\langle \mu_x \rangle$ and $\langle \mu_y \rangle$ involved in the transitions in (147) are imaginary. However, we may simply use, instead, real numbers in the formula because the absolute value of the entire sum is involved.

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5. "3p-COMPLEX" CALCULATIONS FOR THE $\tilde{C}^1B_1$ AND $\tilde{D}^1A_1$ BANDS OF WATER

5.1 THE ROTATIONAL CONSTANTS

The rotation -electronic interaction theory, presented in Chapter 4, includes the various interaction terms explicitly. This requires the use of numerical values for the "deperturbed (ℓ-uncoupled) rotational constants" in the expressions for the energy matrix elements given in TABLES 7 and 8 for the general spin case and the singlet spin case respectively. For a p-complex, $\ell = 1$, the electronic interaction constants λ_{LL} and δ_{LL} must also be specified. We shall ignore the other interaction constants. Those interaction constants which involve spin are not in any case defined for the singlet case in which we are interested. Values for the orbit-rotation constants λ_{LR}, δ_{LR} and γ_{LR} are not available. Values could, of course, be obtained by a non-linear least squares fit to the frequencies of the transitions in the spectra.

5.2 CALCULATIONS OF INTERACTION CONSTANTS

From Eq (7) of Raynes [20] we write the orbit-orbit effects as

$$\lambda_{LL}(3\hat{L}_z^2 - \hat{L}^2) + \delta_{LL}(\hat{L}_x^2 - \hat{L}_y^2) + \mathcal{E}$$
$$= \mathcal{E} - (\lambda_{LL} - \delta_{LL})\hat{L}_x^2 - (\lambda_{LL} + \delta_{LL})\hat{L}_y^2 + 2\lambda_{LL}\hat{L}_z^2 \qquad (148)$$

where we have replaced α and β by λ_{LL} and δ_{LL} respectively and have also included a purely electronic energy $\mathcal{E}$. Creutzberg and Hougen [5] have given an equivalent formulation for the triplet case. This, when written for our

case of L = 1 rather than S = 1, is given by

$$\mathcal{E}_x\,(1-\hat{L}^2_x)+\mathcal{E}_y\,(1-\hat{L}^2_y)+\mathcal{E}_z\,(1-\hat{L}^2_z)$$
$$=\mathcal{E}_x+\mathcal{E}_y+\mathcal{E}_z-\mathcal{E}_x\hat{L}^2_x-\mathcal{E}_y\hat{L}^2_y-\mathcal{E}_z\hat{L}^2_z \qquad (149)$$

On comparing (148) and (149), we find that

$$\mathcal{E}=\mathcal{E}_x+\mathcal{E}_y+\mathcal{E}_z \qquad (150a)$$
$$\mathcal{E}_x=\lambda_{LL}-\delta_{LL} \qquad (150b)$$
$$\mathcal{E}_y=\lambda_{LL}+\delta_{LL} \qquad (150c)$$
$$\mathcal{E}_z=-2\lambda_{LL} \qquad (150d)$$

Then from (150), we find that

$$\mathcal{E}=\mathcal{E}_x+\mathcal{E}_y+\mathcal{E}_z=0 \qquad (151a)$$
$$\lambda_{LL}=\tfrac{1}{2}(\mathcal{E}_x+\mathcal{E}_y)=-\tfrac{1}{2}\mathcal{E}_z \qquad (151b)$$
$$\delta_{LL}=-\tfrac{1}{2}(\mathcal{E}_x-\mathcal{E}_y) \qquad (151c)$$

A redundancy condition such as that given above in (151a) is of course expected since only two parameters, such as λ_{LL} and δ_{LL}, are required to describe the interaction. This redundancy condition permits us to rewrite (151b) and (151c) in terms of electronic energy differences that are experimentally known values. Hence we find that

$$\lambda_{LL}=\frac{\mathcal{E}_x+\mathcal{E}_y+\mathcal{E}_z-3\mathcal{E}_z}{6}=\frac{\mathcal{E}_x+\mathcal{E}_y-2\mathcal{E}_z}{6} \qquad (152a)$$
$$\delta_{LL}=\tfrac{1}{2}(\mathcal{E}_y-\mathcal{E}_x) \qquad (152b)$$

Bell [1] and Johns [11] have given the values of the effective electronic energy differences between the $\tilde{D}^1A_1$, and $\tilde{C}^1B_1$ electronic states and between the $\tilde{D}^1A_1$ and $^1A_2$ electronic states for both H_2O and D_2O ((85a) and (85b) in Chapter 3). Then from (73) one obtains the purely electronic energy differences as follows:

$$\mathcal{E}_x - \mathcal{E}_z = (\mathcal{E}_{eff_x} - \mathcal{E}_{eff_z}) + (B-C) \qquad (153a)$$

$$\mathcal{E}_y - \mathcal{E}_z = (\mathcal{E}_{eff_y} - \mathcal{E}_{eff_z}) + (B-A) \qquad (153b)$$

The expressions (153), on using (85a), (85b) and the numerical values of the deperturbed rotational constants A, B, C (which are represented by A', B', C' in TABLE 4). give the purely electronic energy differences for H_2O and D_2O as follows:

FOR H_2O:

$$\left.\begin{aligned} \mathcal{E}_x - \mathcal{E}_z &= 1438.17 \quad cm^{-1} \\ \mathcal{E}_y - \mathcal{E}_z &= -3602.46 \quad cm^{-1} \\ \mathcal{E}_y - \mathcal{E}_x &= -5040.63 \quad cm^{-1} \end{aligned}\right\} \qquad (154a)$$

FOR D_2O

$$\left.\begin{aligned} \mathcal{E}_x - \mathcal{E}_z &= 1324.93 \quad cm^{-1} \\ \mathcal{E}_y - \mathcal{E}_z &= -2207.04 \quad cm^{-1} \\ \mathcal{E}_y - \mathcal{E}_x &= -3531.97 \quad cm^{-1} \end{aligned}\right\} \qquad (154b)$$

Substitution of the results (154a) in (152) gives the orbit-orbit interaction constants λ_{LL} and δ_{LL} for H_2O. Similarly, the values of λ_{LL} and δ_{LL} for D_2O are obtained by using (154b) in (152). The results are summarized in TABLE 10.

5.3 COMPUTATIONAL DETAILS OF ENERGIES

It has been found convenient to centre the energy levels about the quantum numbers J=0, K=0 and Λ=0. If we add the three diagonal elements corresponding to Λ=0, $\pm$1 for J=0 and K=0 then, the average (i.e., one-third) of such a sum is

$$\left[\tfrac{2}{3}(A+B+C) - 2\gamma_{LR}\right] \qquad (155)$$

This can be verified from the expression for the diagonal matrix elements given in TABLE 8. Thus, on adding $-\left[\frac{2}{3}(A+B+C) - 2\gamma_{LR}\right]$ to the right hand side of the expression for the diagonal matrix elements in TABLE 8, we find that the result for L = 1 is

$$\begin{aligned}\langle JK;\Lambda\Sigma|\hat{H}_{eff}|JK;\Lambda\Sigma\rangle &= \tfrac{1}{2}[A+C][J(J+1)] - \left[\tfrac{A+C}{2} - B\right]K^2 - \left[\left(\tfrac{A+C}{2} - B\right) - 3\lambda_{LL} + 3\lambda_{LR}\right]\Lambda^2 \\ &+ \left[-2B + \gamma_{LR} + 2\lambda_{LR}\right]K\Lambda + \tfrac{2}{3}\left[\tfrac{A+C}{2} - B\right] - 2\lambda_{LL} + 2\lambda_{LR} \qquad (156)\end{aligned}$$

Thus (156), when used as the diagonal matrix elements, centres the energy levels about J = 0 and K = 0.

In order to calculate the rotation-electronic energies for the three electronic states $\tilde{C}^1B_1$, $\tilde{D}^1A_1$ and $^1A_2$ of the 3p-complex of Rydberg, the values of the interaction constants λ_{LR} & γ_{LR} are set to zero because they are not available as yet. A computer programme has been developed which by using the diagonal matrix elements (156) and the off-diagonal elements given in TABLE 8, diagonalizes the matrix to give eigenvalues and eigenvectors for the rotational bands in the three electronic states $\tilde{C}^1B_1$, $\tilde{D}^1A_1$ and $^1A_2$. It is to be noted that because of the presence of three bands, the matrix size for a total quantum number J will be $3\left[(2J+1) \times (2J+1)\right]$. The results are obtained for both H_2O D_2O. True values of the rotational energies in the various electronic states are obtained by adding the appropriate band origins (TABLE 10). Since we have found that the transitions to $^1A_2$ level are very weak compared to those of $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$, the rotational energies for $^1A_2$ electronic state are not listed. The energies of rotation-electronic

states for $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$ bands for H_2O as well as D_2O are listed in Tables IV.1 and IV.2 in APPENDIX IV.

TABLE 10

BAND ORIGINS AND INTERACTION CONSTANTS FOR H_2O AND D_2O

	H_2O	D_2O
Band Origin	79907.0 cm^{-1}	80460.2 cm^{-1}
λ_{LL}	-356.95167 cm^{-1}	-144.64833 cm^{-1}
δ_{LL}	-2500.685 cm^{-1}	-1755.015 cm^{-1}

5.4 COMPUTATIONAL DETAILS OF RELATIVE INTENSITIES OF ELECTRIC DIPOLE TRANSITIONS

Computer programmes for the Burroughs B6700 System have been developed to compute the relative intensities of electric dipole transitions from the ground rotation-electronic states $\tilde{X}^1A_1$ to the p-complex Rydberg states in H_2O and D_2O molecules. That is, transitions from the $\tilde{X}^1A_1$ band to all the three rotational bands in $\tilde{C}^1B_1$, $\tilde{D}^1A_1$ and $^1A_2$ electronic states are considered. The molecular core of H_2O as well as that of D_2O is of symmetry B_1 in both the ground and the excited states. Therefore, the expression (134) for the line strengths and hence the relations (135) for the various ratios of dipole components $\langle \mu_x \rangle$ and $\langle \mu_z \rangle$ are used to calculate the corresponding relative intensities. The numerical values of the eigenvalues and the corresponding eigenvectors used here have been calculated and stored in the initial stage of this programme for both the ground

state $\tilde{X}^1A_1$ and the p-complex Rydberg states. The numerical values of λ_{LL} and δ_{LL} for the final states of H_2O and D_2O used in these calculations are given in TABLE 10, while the values of both the deperturbed rotational constants and the rotational constants in the ground rotation-electronic states $\tilde{X}^1A_1$ are given in TABLE 4 (Chapter 3).

The selection rules are brought into effect by first assigning and storing the symmetry species to the initial and final states, consistent with the criteria given in TABLE 1 (Chapter 2) and TABLE 9 (Chapter 4) respectively, in the form of symmetry codes, established by calling two separate subroutines. It is to be pointed out that the codes for the final states have been assigned such that the molecular species B_1 are included. A third subroutine then changes the already stored symmetry codes of rotational states in the p-complex Rydberg states to those of the initial states for which transitions are allowed as determined by the selection rules (103). The nuclear statistical weights to the energy levels are attached as described in SECTION 3.4 (Chapter3).

The results so obtained for line positions in H_2O and D_2O are listed in TABLES IV.1 and IV.2 respectively. Also, the corresponding relative intensities for $\tilde{C}^1B_1$, $\tilde{D}^1A_1$ bands for the various ratios of electronic dipole moment components are given in TABLES V.1, V.2 for H_2O and in TABLES V.3 and V.4 for D_2O. The relative intensities $[I]^{J''}_{J'} \times 10 < 0.5$ are not listed. The relative intensities of dipole transitions

to the $^1A_2$ electronic state are extremely weak(from 10^{-3} to 10^{-8}) and therefore not listed.

In order to give an overall picture of the rotational line positions and relative intensities in $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$ bands of H_2O, graphical plots of the spectra are carried out in the form of theoretical stick spectra for all the three cases of dipole components' ratios for the $\tilde{C}^1B_1$ band. However, for $\tilde{D}^1A_1$ band , stick spectrum for only one case, viz., $\langle \mu_z \rangle : \langle \mu_x \rangle = 1 : 0$, is plotted because the other cases do not differ appreciably in the values of their relative intensities. This is evident from **TABLE** V.2. Similarly, for D_2O, the relative intensities and line positions listed in **TABLES** V.3 and V.4 can be used to draw the theoretical stick spectra, not shown in this thesis.

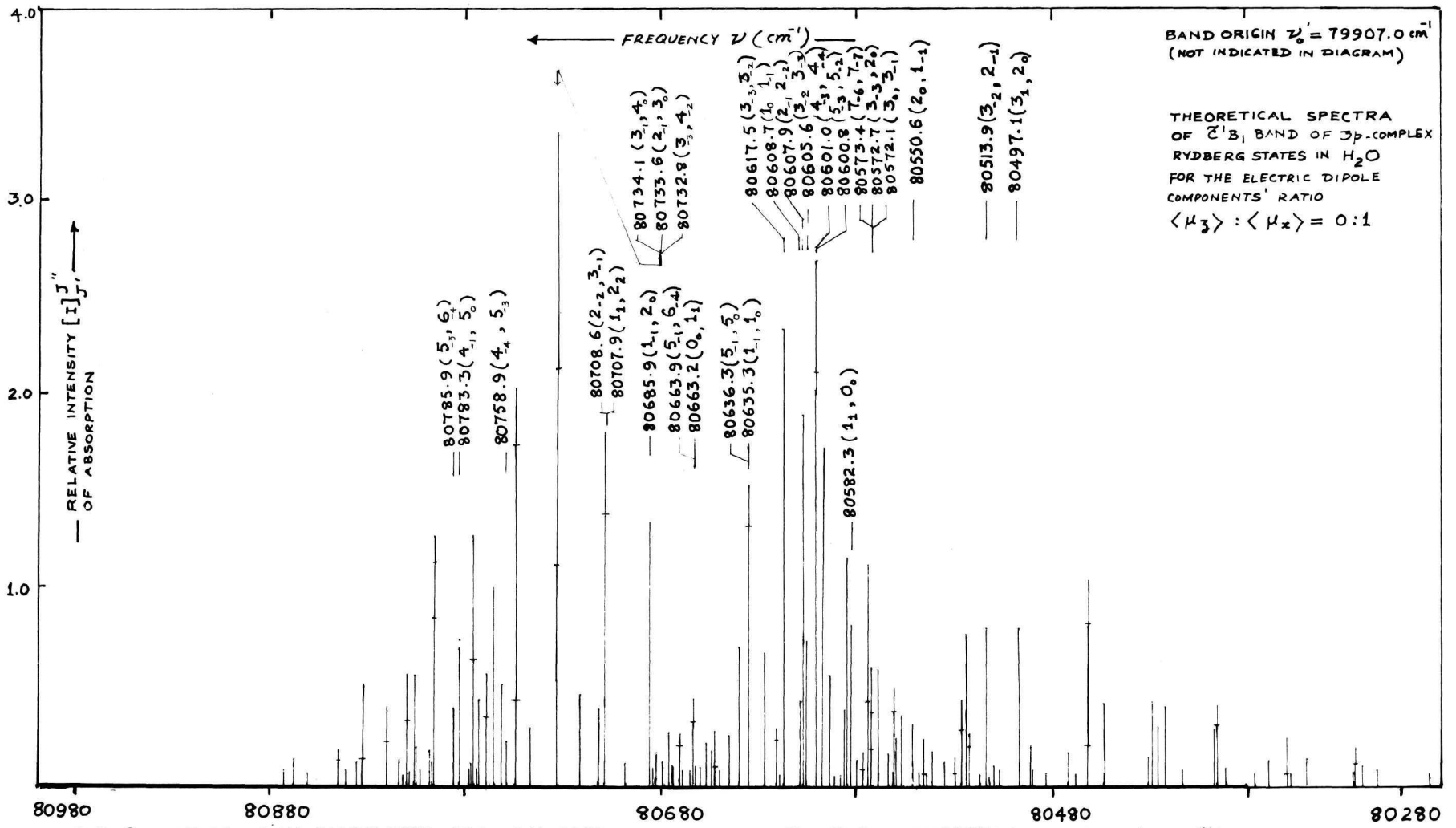

FIG. 4. THEORETICALLY CALCULATED SPECTRAL LINE POSITIONS AND RELATIVE INTENSITIES (ABSORBTION) OF $\tilde{C}\,^1B_1$ ROTATION-ELECTRONIC BAND OF THE 3p-COMPLEX RYDBERG STATES IN H_2O FOR $\langle \mu_z \rangle : \langle \mu_x \rangle = 0:1$. FOR THE PURPOSE OF COMPARISON WITH EXPERIMENTAL RESULTS, IMPORTANT LINE POSITIONS ARE IDENTIFIED EXPLICITLY. THE BRACKETS IDENTIFY THE STATES $(J''_{\tau''}, J'_{\tau'})$ INVOLVED IN A TRANSITION. WHENEVER LINE POSITIONS ARE VERY CLOSE, THEIR INTENSITIES APPEAR ALONG THE SAME VERTICAL LINE, THE LOWEST WAVE NUMBER'S INTENSITY APPEARING AT THE BOTTOM SECTION OF A LINE.

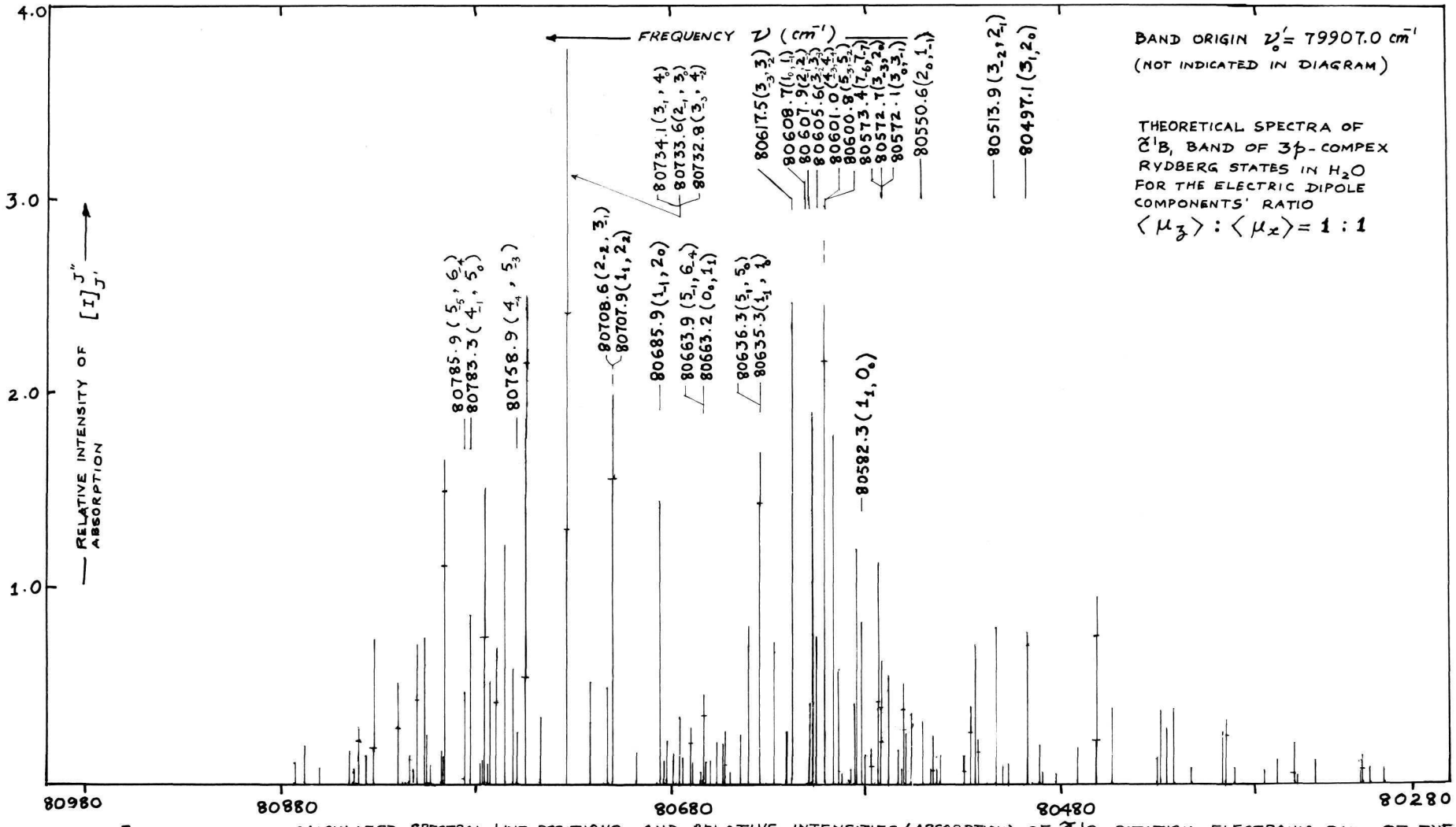

FIG. 5 THEORETICALLY CALCULATED SPECTRAL LINE POSITIONS AND RELATIVE INTENSITIES (ABSORPTION) OF $\tilde{C}\,^1B_1$ ROTATION-ELECTRONIC BAND OF THE 3p-COMPLEX RYDBERG STATES IN H_2O FOR $\langle \mu_z \rangle : \langle \mu_x \rangle = 1:1$.

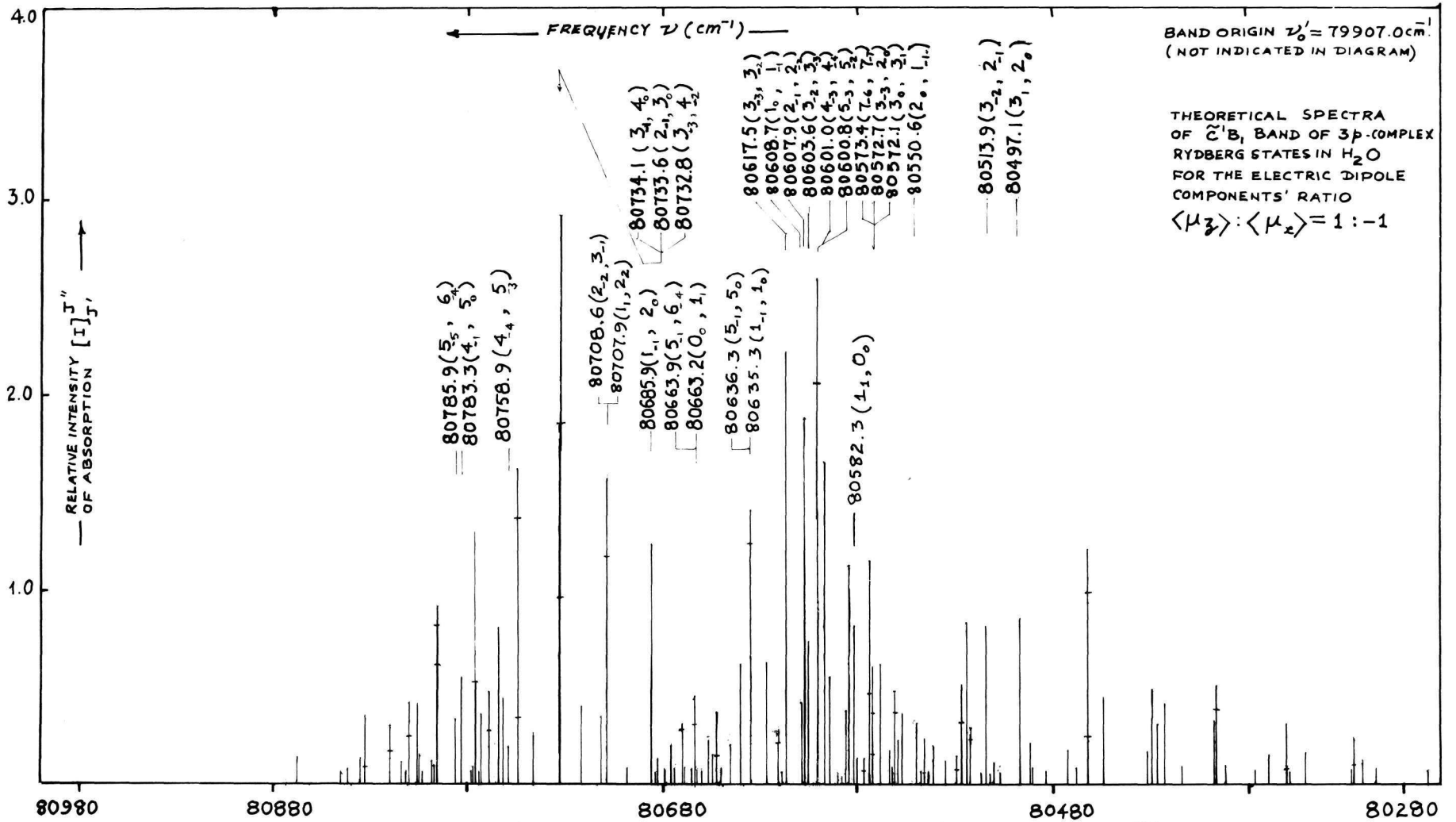

FIG. 6. THEORETICALLY CALCULATED SPECTRAL LINE POSITIONS AND RELATIVE INTENSITIES (ABSORPTION) OF $\tilde{C}\,^1B_1$ ROTATION-ELECTRONIC BAND OF THE 3p-COMPLEX RYDBERG STATE IN H_2O FOR $\langle \mu_z \rangle : \langle \mu_x \rangle = 1 : -1$.

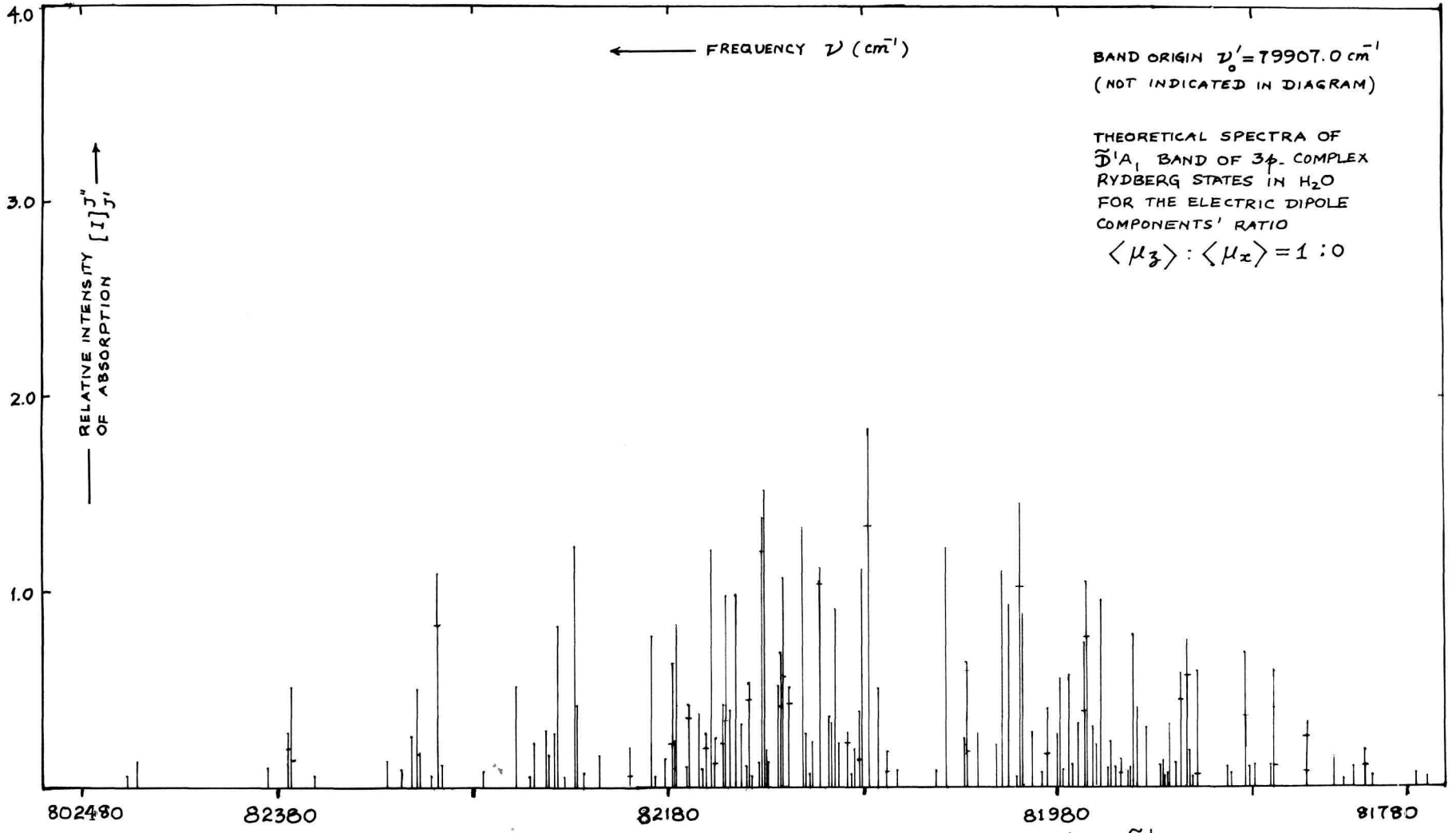

FIG.7. THEORETICALLY CALCULATED SPECTRAL LINE POSITIONS AND RELATIVE INTENSITIES(ABSORPTION) OF $\tilde{D}\,^1A_1$ ROTATION-ELECTRONIC BAND OF THE 3p-COMPLEX RYDBERG STATE IN WATER FOR $\langle \mu_z \rangle : \langle \mu_x \rangle = 1 : 0$

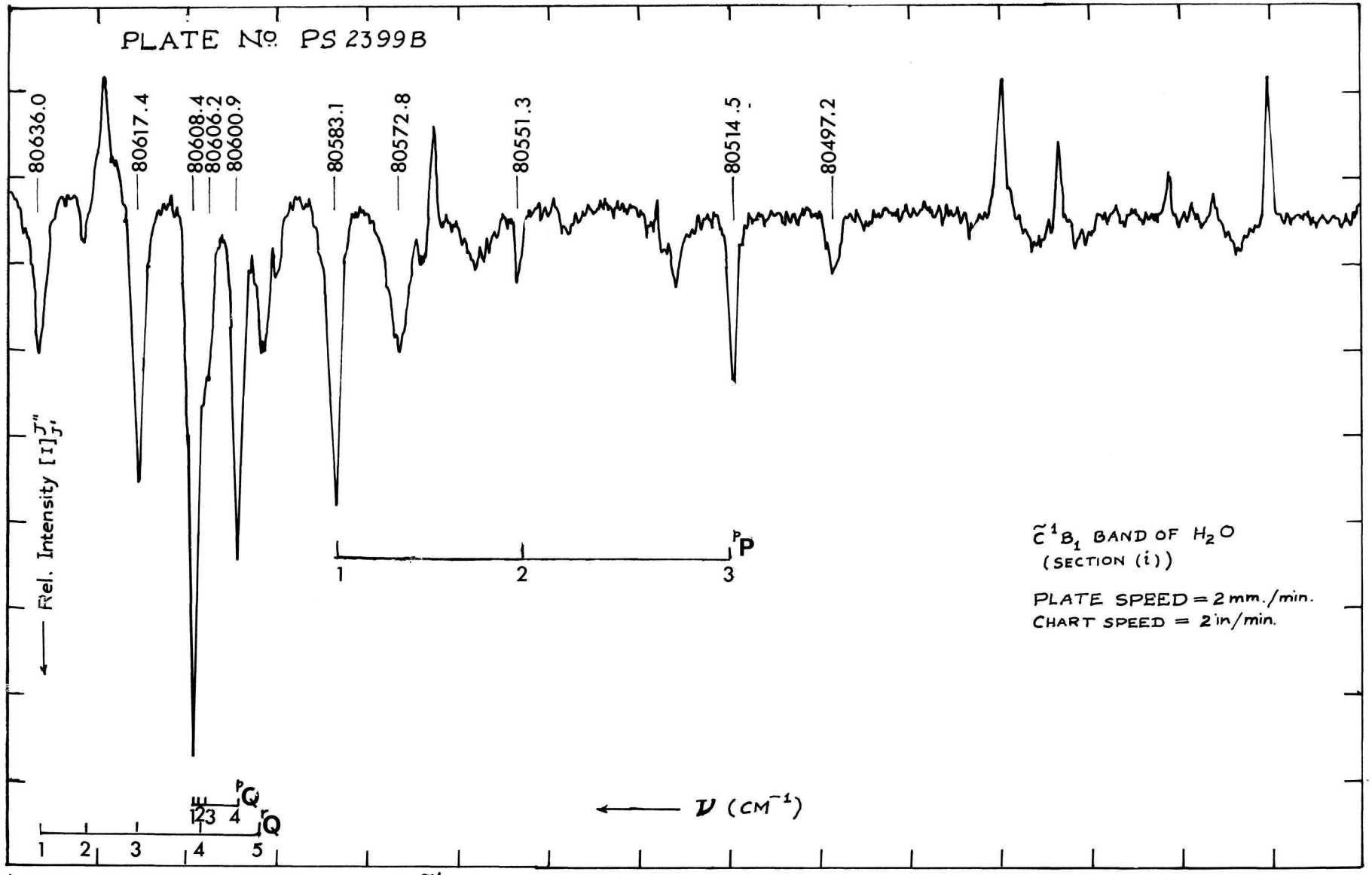

FIG. 8(a). EXPERIMENTAL SPECTRA OF THE $\tilde{C}^{1}B_{1}$ BAND OF H_2O. THE SPECTRA WERE REPRODUCED ON A MICRODENSITOMETER FROM THE PHOTOGRAPHIC PLATE. (COURTESY OF DR. J.W.C. JOHNS OF HERZBERG INSTITUTE OF ASTROPHYSICS, NATIONAL RESEARCH COUNCIL, CANADA).

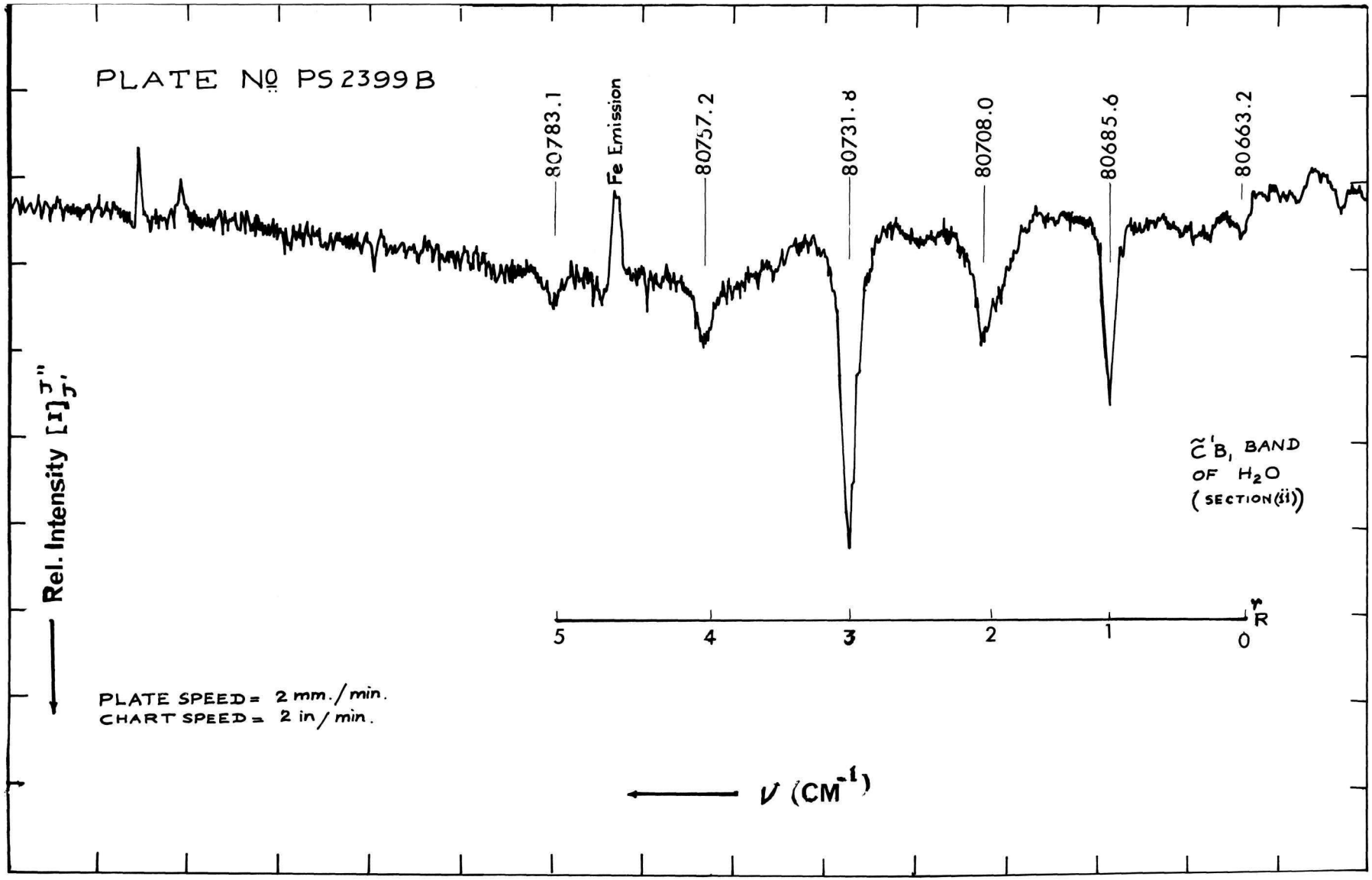

FIG 8(b). EXPERIMENTAL SPECTRA OF THE $\tilde{C}\,^1B_1$ BAND OF H_2O. THE SPECTRA WERE REPRODUCED ON A MICRODENSITOMETER FROM THE PHOTOGRAPHIC PLATE (COURTESY OF DR. J. W. C. JOHNS OF HERZBERG INSTITUTE OF ASTROPHYSICS, NATIONAL RESEARCH COUNCIL, CANADA).

6. DISCUSSION OF THE RESULTS AND CONCLUSIONS

The results of the application of our theory to H_2O and D_2O are listed in TABLES IV.1, IV.2, V.1, V.2, V.3 and V.4. These results, on comparing with those given in TABLES II.1, II.2, III.1, III.2, III.3 and III.4, indicate that the line positions can be predicted to about the same accuracy by using the approximate method similar to that used by Creutzberg and Hougen[5]. This situation arises because the electronic levels in the p -complex are separated well enough so that the interactions among them is weak.

Approximate calculations of relative intensities assuming no interactions, are really not distinguishable from those of any of the three limiting cases of dipole components' ratios. There is, however, some evidence of interference effect. That is, some branches are slightly enhanced and some slightly weakened in their relative intensities when comparing one case to another. The effect can be expected to be enhanced when strong interactions are involved. However, for weak interactions, we see that the intensities show little departure from the usual rigid rotor case where no interactions are assumed.

Our results are also presented in the form of theoretical stick spectra, given by FIGS. 4,5, 6 and 7, along with the experimental results supplied by

Dr. J.W.C. Johns (Private communication [24]) for the $\tilde{C}^1B_1$ band of H_2O, shown in FIG.8. Comparison of the theoretical and experimental spectra seems to show a qualitative agreement. Agreement is close, as should be, since the logarithmic response of the photographic plate, used to record the spectrum, tends to compensate for the exponential absorption law so that the intensities should be roughly proportional to the absorption coefficients or line strengths and is thus comparable to our calculated relative intensities.

It is, however, very clear that if calculations are carried out for higher Rydberg states (e.g., $\ell=1$, $\ell=2$, $\ell=3$, etc.) the interactions are expected to become more and more significant with increasing ℓ values, and the effect will appear in terms of changes in the intensity distribution. Therefore, in view of the present findings , it is suggested that calculations of energies and relative intensities be carried out in order to see the real effects of the interactions involved.

APPENDIX I

TABLE I.1

Character Table of the C_{2V} Point Group

C_{2V}	$\hat{E}$	$\hat{C}_{2z}$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz) \equiv \hat{\sigma}_v'$		
A_1	1	1	1	1		μ_z
A_2	1	1	-1	-1	R_z	$\vec{\mu}$ (SPACE FIXED)
B_1	1	-1	1	-1	R_y	μ_x
B_2	1	-1	-1	1	R_x	μ_y

APPENDIX II

TABLE II.1

Rotation-Electronic Enery Levels of the $\tilde{X}\,^1A_1$, $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$ States of H_2O

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
0_0	000.00	0_0	80624.70	0_0	82058.70
1_{-1}	023.80	1_{-1}	0645.89	1_{-1}	2079.94
1_0	037.16	1_0	0659.15	1_0	2097.47
1_1	042.39	1_1	0663.24	1_1	2101.77
2_{-2}	070.13	2_{-2}	0687.46	2_{-2}	2121.71
2_{-1}	079.53	2_{-1}	0697.44	2_{-1}	2135.65
2_0	095.21	2_0	0709.71	2_0	2148.54
2_1	135.31	2_1	0749.49	2_1	2201.15
2_2	136.56	2_2	0750.30	2_2	2201.85
3_{-3}	136.91	3_{-3}	0747.98	3_{-3}	2182.75
3_{-2}	142.37	3_{-2}	0754.41	3_{-2}	2192.51
3_{-1}	173.54	3_{-1}	0778.85	3_{-1}	2218.22
3_0	206.70	3_0	0813.06	3_0	2264.86
3_1	212.57	3_1	0816.92	3_1	2268.23
3_2	287.30	3_2	0890.05	3_2	2363.68
3_3	287.49	3_3	0890.15	3_3	2363.76
4_{-4}	222.37	4_{-4}	0826.05	4_{-4}	2261.61
4_{-3}	225.07	4_{-3}	0829.63	4_{-3}	2267.66

APPX II

TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
$J''_{\tau''}$	$E''(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$
4_{-2}	276.01	4_{-2}	80869.83	4_{-2}	82310.14
4_{-1}	300.89	4_{-1}	0897.19	4_{-1}	2349.26
4_{0}	316.47	4_{0}	0907.73	4_{0}	2358.72
4_{1}	384.52	4_{1}	0976.17	4_{1}	2449.84
4_{2}	385.85	4_{2}	0976.87	4_{2}	2450.33
4_{3}	494.62	4_{3}	1082.12	4_{3}	2586.56
4_{4}	494.64	4_{4}	1082.13	4_{4}	2586.57
5_{-5}	325.90	5_{-5}	0920.91	5_{-5}	2357.31
5_{-4}	327.10	5_{-4}	0922.71	5_{-4}	2360.70
5_{-3}	400.58	5_{-3}	0981.39	5_{-3}	2423.24
5_{-2}	417.10	5_{-2}	1001.34	5_{-2}	2453.90
5_{-1}	447.92	5_{-1}	1022.89	5_{-1}	2473.80
5_{0}	506.19	5_{0}	1084.00	5_{0}	2557.77
5_{1}	511.10	5_{1}	1086.67	5_{1}	2559.69
5_{2}	616.38	5_{2}	1189.86	5_{2}	2694.29
5_{3}	616.61	5_{3}	1189.95	5_{3}	2694.35
5_{4}	757.63	5_{4}	1325.95	5_{4}	2870.02
5_{5}	757.63	5_{5}	1325.95	5_{5}	2870.02
6_{-6}	447.60	6_{-6}	1032.48	6_{-6}	2469.53
6_{-5}	448.09	6_{-5}	1033.32	6_{-5}	2471.30

APPX II

TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
$J''_{\tau''}$	$E''(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$
6_{-4}	0544.85	6_{-4}	81111.85	6_{-4}	82556.09
6_{-3}	0554.43	6_{-3}	1124.94	6_{-3}	2578.24
6_{-2}	0605.51	6_{-2}	1161.68	6_{-2}	2613.13
6_{-1}	0651.86	6_{-1}	1213.34	6_{-1}	2687.36
6_{0}	0664.83	6_{0}	1220.69	6_{0}	2692.81
6_{1}	0763.19	6_{1}	1319.64	6_{1}	2824.02
6_{2}	0764.25	6_{2}	1320.10	6_{2}	2824.29
6_{3}	0903.63	6_{3}	1455.14	6_{3}	2999.21
6_{4}	0903.66	6_{4}	1455.15	6_{4}	2999.21
6_{5}	1076.38	6_{5}	1621.58	6_{5}	3214.08
6_{6}	1076.38	6_{6}	1621.58	6_{6}	3214.08
7_{-7}	0587.64	7_{-7}	1160.89	7_{-7}	2598.32
7_{-6}	0587.83	7_{-6}	1161.26	7_{-6}	2599.20
7_{-5}	0707.15	7_{-5}	1259.65	7_{-5}	2707.06
7_{-4}	0712.07	7_{-4}	1267.36	7_{-4}	2721.71
7_{-3}	0787.12	7_{-3}	1322.86	7_{-3}	2775.78
7_{-2}	0820.81	7_{-2}	1363.79	7_{-2}	2838.36
7_{-1}	0847.67	7_{-1}	1379.86	7_{-1}	2850.78
7_{0}	0935.09	7_{0}	1471.57	7_{0}	2975.90
7_{1}	0938.72	7_{1}	1473.19	7_{1}	2976.86
7_{2}	1074.74	7_{2}	1606.38	7_{2}	3150.36

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TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\ ^1A_1$		EXCITED STATE $\tilde{C}\ ^1B_1$		EXCITED STATE $\tilde{D}\ ^1A_1$	
$J''\tau''$	$E''(cm^{-1})$	$J'\tau'$	$E'(cm^{-1})$	$J'\tau'$	$E'(cm^{-1})$
7_3	1074.92	7_3	81606.44	7_3	83150.39
7_4	1246.58	7_4	1772.21	7_4	3364.72
7_5	1246.58	7_5	1772.21	7_5	3364.72
7_6	1450.89	7_6	1969.01	7_6	3618.75
7_7	1450.89	7_7	1969.01	7_7	3618.75
8_{-8}	0746.15	8_{-8}	1306.26	8_{-8}	2743.82
8_{-7}	0746.22	8_{-7}	1306.42	8_{-7}	2744.23
8_{-6}	0887.02	8_{-6}	1423.91	8_{-6}	2874.84
8_{-5}	0889.32	8_{-5}	1428.05	8_{-5}	2883.74
8_{-4}	0990.14	8_{-4}	1504.80	8_{-4}	2960.42
8_{-3}	1012.13	8_{-3}	1534.79	8_{-3}	3010.31
8_{-2}	1058.75	8_{-2}	1564.27	8_{-2}	3034.27
8_{-1}	1131.88	8_{-1}	1645.64	8_{-1}	3150.00
8_0	1141.57	8_0	1650.16	8_0	3152.74
8_1	1271.23	8_1	1779.86	8_1	3323.68
8_2	1271.99	8_2	1780.13	8_2	3323.81
8_3	1441.83	8_3	1944.84	8_3	3537.28
8_4	1441.86	8_4	1944.85	8_4	3537.28
8_5	1645.29	8_5	2141.09	8_5	3790.84
8_6	1645.29	8_6	2141.09	8_6	3790.84
8_7	1881.16	8_7	2368.24	8_7	4084.02

APPX II

TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
$J''_{\tau''}$	E'' (cm^{-1})	$J'_{\tau'}$	E' (cm^{-1})	$J_{\tau'}$	E' (cm^{-1})
8_8	1881.16	8_8	82368.24	8_8	84084.02
9_{-9}	0923.18	9_{-9}	1468.66	9_{-9}	2906.12
9_{-8}	0923.21	9_{-8}	1468.73	9_{-8}	2906.31
9_{-7}	1084.69	9_{-7}	1604.49	9_{-7}	3058.79
9_{-6}	1085.70	9_{-6}	1606.56	9_{-6}	3063.82
9_{-5}	1212.03	9_{-5}	1705.59	9_{-5}	3165.42
9_{-4}	1224.83	9_{-4}	1725.68	9_{-4}	3202.66
9_{-3}	1296.07	9_{-3}	1773.05	9_{-3}	3243.12
9_{-2}	1353.00	9_{-2}	1841.62	9_{-2}	3346.26
9_{-1}	1374.21	9_{-1}	1852.15	9_{-1}	3352.90
9_0	1493.27	9_0	1975.76	9_0	3519.35
9_1	1495.76	9_1	1976.67	9_1	3519.80
9_2	1662.42	9_2	2139.65	9_2	3731.93
9_3	1662.55	9_3	2139.69	9_3	3731.94
9_4	1864.68	9_4	2335.12	9_4	3984.82
9_5	1864.68	9_5	2335.12	9_5	3984.82
9_6	2099.76	9_6	2561.77	9_6	4277.58
9_7	2099.76	9_7	2561.77	9_6	4277.58
9_8	2367.18	9_8	2819.27	9_8	4609.90
9_9	2367.18	9_9	2819.27	9_9	4609.90
10_{-10}	1118.77	10_{-10}	1648.12	10_{-10}	3085.29

TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
$J''_{\tau''}$	$E''(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$
10_{-9}	1118.78	10_{-9}	81648.15	10_{-9}	83085.38
10_{-8}	1300.49	10_{-8}	1801.59	10_{-8}	3258.86
10_{-7}	1300.91	10_{-7}	1802.57	10_{-7}	3261.55
10_{-6}	1451.26	10_{-6}	1923.49	10_{-6}	3388.95
10_{-5}	1457.98	10_{-5}	1935.75	10_{-5}	3414.76
10_{-4}	1556.99	10_{-4}	2004.68	10_{-4}	3476.36
10_{-3}	1597.63	10_{-3}	2059.11	10_{-3}	3564.44
10_{-2}	1636.84	10_{-2}	2080.07	10_{-2}	3578.44
10_{-1}	1740.83	10_{-1}	2194.18	10_{-1}	3737.53
10_{0}	1747.57	10_{0}	2196.75	10_{0}	3738.81
10_{1}	1908.63	10_{1}	2356.84	10_{1}	3948.85
10_{2}	1909.15	10_{2}	2356.99	10_{2}	3948.91
10_{3}	2109.30	10_{3}	2551.27	10_{3}	4200.83
10_{4}	2109.33	10_{4}	2551.27	10_{4}	4200.83
10_{5}	2343.31	10_{5}	2777.22	10_{5}	4492.99
10_{6}	2343.31	10_{6}	2777.22	10_{6}	4492.99
10_{7}	2609.99	10_{7}	3034.26	10_{7}	4824.92
10_{8}	2609.99	10_{8}	3034.26	10_{8}	4824.92
10_{9}	2908.96	10_{9}	3322.10	10_{9}	5196.38
10_{10}	2908.96	10_{10}	3322.10	10_{10}	5196.38
11_{-11}	1332.91	11_{-11}	1844.67	11_{-11}	3281.37

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TABLE II.1 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
$J''_{\tau''}$	$E''(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$	$J'_{\tau'}$	$E'(cm^{-1})$
11_{-10}	1332.92	11_{-10}	81844.68	11_{-10}	83281.41
11_{-9}	1534.63	11_{-9}	2015.44	11_{-9}	3475.26
11_{-8}	1534.81	11_{-8}	2015.89	11_{-8}	3476.65
11_{-7}	1707.58	11_{-7}	2157.49	11_{-7}	3629.39
11_{-6}	1710.83	11_{-6}	2164.37	11_{-6}	3645.97
11_{-5}	1838.51	11_{-5}	2257.26	11_{-5}	3732.52
11_{-4}	1864.77	11_{-4}	2297.51	11_{-4}	3804.13
11_{-3}	1928.04	11_{-3}	2333.99	11_{-3}	3830.19
11_{-2}	2013.57	11_{-2}	2435.08	11_{-2}	3978.31
11_{-1}	2029.06	11_{-1}	2441.35	11_{-1}	3981.52
11_{0}	2180.72	11_{0}	2596.62	11_{0}	4188.23
11_{1}	2182.35	11_{1}	2597.11	11_{1}	4188.42
11_{2}	2379.45	11_{2}	2789.70	11_{2}	4439.01
11_{3}	2379.54	11_{3}	2789.72	11_{3}	4439.02
11_{4}	2612.01	11_{4}	3014.73	11_{4}	4730.39
11_{5}	2612.01	11_{5}	3014.73	11_{5}	4730.39
11_{6}	2877.71	11_{6}	3271.14	11_{6}	5061.78
11_{7}	2877.71	11_{7}	3271.14	11_{7}	5061.78
11_{8}	3175.98	11_{8}	3558.54	11_{8}	5432.87
11_{9}	3175.98	11_{9}	3558.54	11_{9}	5432.87
11_{10}	3506.49	11_{10}	3876.73	11_{10}	5843.47
11_{11}	3506.49	11_{11}	3876.73	11_{11}	5843.47

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TABLE II.2

Rotation-Electronic Energy Levels of the $\tilde{X}\,^1A_1$, $\tilde{C}\,^1B_1$ and $\tilde{D}\,^1A_1$ States of D_2O

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
0_0	000.00	0_0	80751.90	0_0	82074.90
1_{-1}	012.12	1_{-1}	0762.63	1_{-1}	2085.64
1_0	020.23	1_0	0770.96	1_0	2095.34
1_1	022.65	1_1	0772.85	1_1	2097.32
2_{-2}	035.90	2_{-2}	0783.80	2_{-2}	2106.83
2_{-1}	042.05	2_{-1}	0790.53	2_{-1}	2114.84
2_0	049.31	2_0	0796.20	2_0	2120.76
2_1	073.64	2_1	0821.19	2_1	2149.88
2_2	074.11	2_2	0821.48	2_2	2150.16
3_{-3}	070.50	3_{-3}	0814.89	3_{-3}	2137.98
3_{-2}	074.51	3_{-2}	0819.72	3_{-2}	2143.92
3_{-1}	088.98	3_{-1}	0831.03	3_{-1}	2155.75
3_0	110.00	3_0	0853.38	3_0	2182.09
3_1	112.22	3_1	0854.77	3_1	2183.42
3_2	156.87	3_2	0899.92	3_2	2235.72
3_3	156.93	3_3	0899.95	3_3	2235.75
4_{-4}	115.09	4_{-4}	0855.27	4_{-4}	2178.47
4_{-3}	117.37	4_{-3}	0858.36	4_{-3}	2182.43

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TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
4_{-2}	141.18	4_{-2}	80877.07	4_{-2}	82202.02
4_{-1}	158.12	4_{-1}	0896.08	4_{-1}	2224.82
4_0	164.22	4_0	0900.01	4_0	2228.60
4_1	206.13	4_1	0943.34	4_1	2279.15
4_2	206.52	4_2	0943.53	4_2	2279.31
4_3	270.69	4_3	1007.82	4_3	2353.58
4_4	270.69	4_4	1007.83	4_4	2353.58
5_{-5}	169.22	5_{-5}	0904.49	5_{-5}	2227.79
5_{-4}	170.38	5_{-4}	0906.28	5_{-4}	2230.2
5_{-3}	205.18	5_{-3}	0933.89	5_{-3}	2259.19
5_{-2}	217.68	5_{-2}	0949.09	5_{-2}	2277.89
5_{-1}	230.21	5_{-1}	0957.43	5_{-1}	2286.02
5_0	267.83	5_0	0997.72	5_0	2333.53
5_1	269.32	5_1	0998.46	5_1	2334.18
5_2	332.32	5_2	1062.11	5_2	2407.86
5_3	332.37	5_3	1062.13	5_3	2407.88
5_4	415.24	5_4	1145.00	5_4	2503.56
5_5	415.24	5_5	1145.00	5_5	2503.56
6_{-6}	232.82	6_{-6}	0962.37	6_{-6}	2285.71

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
6_{-5}	233.37	6_{-5}	80963.34	6_{-5}	82287.07
6_{-4}	280.04	6_{-4}	1000.91	6_{-4}	2326.70
6_{-3}	288.36	6_{-3}	1012.20	6_{-3}	2341.10
6_{-2}	309.81	6_{-2}	1026.96	6_{-2}	2355.65
6_{-1}	341.84	6_{-1}	1063.03	6_{-1}	2398.87
6_{0}	345.98	6_{0}	1065.15	6_{0}	2400.72
6_{1}	406.56	6_{1}	1127.44	6_{1}	2473.18
6_{2}	406.81	6_{2}	1127.54	6_{2}	2473.25
6_{3}	489.15	6_{3}	1210.10	6_{3}	2568.65
6_{4}	489.15	6_{4}	1210.10	6_{4}	2568.65
6_{5}	590.56	6_{5}	1311.45	6_{5}	2685.65
6_{6}	590.56	6_{6}	1311.45	6_{6}	2685.65
7_{-7}	305.95	7_{-7}	1028.92	7_{-7}	2352.19
7_{-6}	306.20	7_{-6}	1029.42	7_{-6}	2352.92
7_{-5}	364.80	7_{-5}	1077.44	7_{-5}	2403.89
7_{-4}	369.79	7_{-4}	1085.17	7_{-4}	2414.19
7_{-3}	402.32	7_{-3}	1108.24	7_{-3}	2437.22
7_{-2}	427.95	7_{-2}	1139.17	7_{-2}	2475.08
7_{-1}	437.07	7_{-1}	1144.06	7_{-1}	2479.41

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
7_0	493.48	7_0	81203.89	7_0	82549.61
7_1	494.37	7_1	1204.23	7_1	2549.88
7_2	575.66	7_2	1286.24	7_2	2644.77
7_3	575.69	7_3	1286.25	7_3	2644.78
7_4	676.73	7_4	1387.37	7_4	2761.57
7_5	676.73	7_5	1387.37	7_5	2761.57
7_6	796.64	7_6	1507.18	7_6	2899.88
7_7	796.64	7_7	1507.18	7_7	2899.88
8_{-8}	388.69	8_{-8}	1104.19	8_{-8}	2427.29
8_{-7}	388.80	8_{-7}	1104.34	8_{-7}	2427.67
8_{-6}	458.91	8_{-6}	1162.86	8_{-6}	2490.10
8_{-5}	461.64	8_{-5}	1167.74	8_{-5}	2496.94
8_{-4}	506.79	8_{-4}	1200.74	8_{-4}	2530.24
8_{-3}	525.84	8_{-3}	1225.96	8_{-3}	2562.01
8_{-2}	542.70	8_{-2}	1235.53	8_{-2}	2570.66
8_{-1}	593.09	8_{-1}	1291.49	8_{-1}	2637.19
8_0	595.57	8_0	1292.48	8_0	2637.98
8_1	674.90	8_1	1373.48	8_1	2731.99
8_2	675.04	8_2	1373.53	8_2	2732.02

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
8_3	0775.47	8_3	81474.30	8_3	82848.48
8_4	0775.48	8_4	1474.31	8_4	2848.49
8_5	0895.07	8_5	1593.92	8_5	2986.61
8_6	0895.07	8_6	1593.92	8_6	2986.61
8_7	1033.48	8_7	1732.19	8_7	3146.23
8_8	1033.48	8_8	1732.19	8_8	3146.23
9_{-9}	0481.09	9_{-9}	1188.23	9_{-9}	2511.05
9_{-8}	0481.13	9_{-8}	1188.35	9_{-8}	2511.25
9_{-7}	0562.26	9_{-7}	1256.84	9_{-7}	2584.87
9_{-6}	0563.65	9_{-6}	1259.70	9_{-6}	2589.11
9_{-5}	0622.13	9_{-5}	1303.78	9_{-5}	2634.09
9_{-4}	0635.11	9_{-4}	1323.18	9_{-4}	2659.46
9_{-3}	0662.40	9_{-3}	1339.60	9_{-3}	2674.62
9_{-2}	0705.26	9_{-2}	1390.23	9_{-2}	2735.95
9_{-1}	0711.07	9_{-1}	1392.66	9_{-1}	2737.90
9_0	0786.97	9_0	1471.92	9_0	2830.38
9_1	0787.45	9_1	1472.07	9_1	2830.49
9_2	0886.91	9_2	1572.32	9_2	2946.47
9_3	0886.93	9_3	1572.32	9_3	2946.47

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
9_4	1006.06	9_4	1691.66	9_4	3084.34
9_5	1006.06	9_5	1691.66	9_5	3084.34
9_6	1144.18	9_6	1829.76	9_6	3243.78
9_7	1144.18	9_7	1829.76	9_7	3243.78
9_8	1301.07	9_8	1986.49	9_8	3424.70
9_9	1301.07	9_9	1986.49	9_9	3424.70
10_{-10}	0583.16	10_{-10}	1281.07	10_{-10}	2603.43
10_{-9}	0583.18	10_{-9}	1281.13	10_{-9}	2603.62
10_{-8}	0674.94	10_{-8}	1359.27	10_{-8}	2688.01
10_{-7}	0675.61	10_{-7}	1360.87	10_{-7}	2690.50
10_{-6}	0747.30	10_{-6}	1416.62	10_{-6}	2748.06
10_{-5}	0755.38	10_{-5}	1430.57	10_{-5}	2767.18
10_{-4}	0795.35	10_{-4}	1455.95	10_{-4}	2791.11
10_{-3}	0829.78	10_{-3}	1500.04	10_{-3}	2845.84
10_{-2}	0841.46	10_{-2}	1505.24	10_{-2}	2850.08
10_{-1}	0911.94	10_{-1}	1581.63	10_{-1}	2940.03
10_0	0913.31	10_0	1582.06	10_0	2940.34
10_1	1011.15	10_1	1681.48	10_1	3055.59
10_2	1011.23	10_2	1681.50	10_2	3055.60

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
10_3	1129.70	10_3	81800.45	10_3	83193.10
10_4	1129.70	10_4	1800.45	10_4	3193.10
10_5	1267.42	10_5	1938.31	10_5	3352.32
10_6	1267.42	10_6	1938.31	10_6	3352.32
10_7	1424.05	10_7	2094.87	10_7	3533.08
10_8	1424.05	10_8	2094.87	10_8	3533.08
10_9	1599.43	10_9	2270.06	10_9	3735.30
10_{10}	1599.43	10_{10}	2270.06	10_{10}	3735.30
11_{-11}	0694.93	11_{-11}	1382.74	11_{-11}	2704.73
11_{-10}	0694.93	11_{-10}	1382.76	11_{-10}	2704.78
11_{-9}	0797.10	11_{-9}	1470.25	11_{-9}	2799.55
11_{-8}	0797.41	11_{-8}	1471.10	11_{-8}	2800.95
11_{-7}	0881.62	11_{-7}	1538.50	11_{-7}	2871.36
11_{-6}	0886.25	11_{-6}	1547.85	11_{-6}	2884.88
11_{-5}	0940.43	11_{-5}	1584.01	11_{-5}	2919.68
11_{-4}	0966.30	11_{-4}	1620.76	11_{-4}	2966.74
11_{-3}	0986.83	11_{-3}	1630.64	11_{-3}	2974.97
11_{-2}	1049.81	11_{-2}	1702.64	11_{-2}	3061.00
11_{-1}	1053.17	11_{-1}	1703.74	11_{-1}	3061.79

APPX II

TABLE II.2 (Continued)

GROUND STATE $\tilde{X}\,^1A_1$		EXCITED STATE $\tilde{C}\,^1B_1$		EXCITED STATE $\tilde{D}\,^1A_1$	
Energy Level $J''_{\tau''}$	Energy $E''(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$	Energy Level $J'_{\tau'}$	Energy $E'(cm^{-1})$
11_0	1148.32	11_0	1801.88	11_0	3175.92
11_1	1148.58	11_1	1801.94	11_1	3175.96
11_2	1266.09	11_2	1920.36	11_2	3312.96
11_3	1266.10	11_3	1920.36	11_3	3312.96
11_4	1403.28	11_4	2057.89	11_4	3471.88
11_5	1403.28	11_5	2059.89	11_5	3471.88
11_6	1559.55	11_6	2214.24	11_6	3652.43
11_7	1559.55	11_7	2214.24	11_7	3652.43
11_8	1734.68	11_8	2389.27	11_8	3854.50
11_9	1734.68	11_9	2389.27	11_9	3854.50
11_{10}	1928.55	11_{10}	2582.91	11_{10}	4078.02
11_{11}	1928.55	11_{11}	2582.91	11_{11}	4078.02

APPENDIX III

TABLE III.1

$\tilde{C}^1B_1$ Transitions in H_2O Calculated for $\langle \mu_x \rangle = 1$

(No electronic interactions)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R	0_0	1_1	80663.2	3.3
P	1_1	0_0	582.3	8.1
Q				
	1_0	1_{-1}	608.7	4.2
	1_{-1}	1_0	635.4	13.3
R				
	1_1	2_{-2}	645.1	2.6
	1_{-1}	2_0	685.9	13.3
	1_1	2_2	707.9	13.7
	1_0	2_1	712.3	4.2
P				
	2_1	1_0	523.8	7.7
	2_2	1_1	526.7	2.9
	2_0	1_{-1}	550.7	3.1
	2_{-2}	1_1	593.1	0.7
Q				
	2_2	2_{-2}	560.9	0.8
	2_1	2_0	574.4	4.3
	2_{-1}	2_{-2}	607.9	19.0
	2_{-2}	2_{-2}	627.3	6.8
	2_0	2_1	654.3	1.7
	2_{-1}	2_2	670.8	3.6

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included in this table.

APPX III

TABLE III.1 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10
R				
	2_1	3_{-2}	80619.1	0.5
	2_0	3_{-3}	652.8	0.9
	2_{-2}	3_{-1}	708.7	4.3
	2_0	3_1	721.7	4.6
	2_{-1}	3_0	733.5	11.3
	2_2	3_3	753.6	4.4
	2_1	3_2	754.7	13.2
P				
	3_2	2_1	462.2	2.1
	3_3	2_2	462.8	6.4
	3_0	2_{-2}	490.7	2.0
	3_1	2_0	497.1	8.1
	3_{-1}	2_{-2}	513.9	8.0
	3_{-3}	2_0	572.8	1.8
	3_{-1}	2_2	576.8	0.8
Q				
	3_3	3_0	525.6	1.7
	3_2	3_1	529.6	0.6
	3_1	3_{-2}	541.8	1.7
	3_0	3_{-1}	572.2	2.0
	3_{-2}	3_{-3}	605.6	7.4
	3_{-3}	3_{-2}	617.5	23.5
	3_{-1}	3_0	639.5	7.1
	3_{-2}	3_1	674.5	1.0
	3_1	3_2	677.5	2.6

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'} \times 10$
	3_0	3_3	80683.5	0.9
R				
	3_1	4_{-4}	652.5	1.8
	3_1	4_{-2}	657.3	2.1
	3_{-3}	4_{-2}	732.9	10.0
	3_{-1}	4_0	734.2	12.2
	3_{-2}	4_{-1}	754.8	3.0
	3_1	4_2	764.3	10.1
	3_0	4_1	769.5	3.4
	3_3	4_4	794.6	8.7
	3_2	4_3	794.8	2.9
P				
	4_3	3_2	395.4	3.2
	4_4	3_3	395.5	1.1
	4_1	3_0	428.5	4.3
	4_2	3_1	431.1	1.5
	4_{-1}	3_{-2}	453.5	4.2
	4_0	3_{-1}	462.4	2.1
	4_{-2}	3_{-3}	472.0	1.8
	4_{-3}	3_0	588.0	0.5
Q				
	4_3	4_2	482.2	0.7
	4_2	4_{-1}	511.3	0.5
	4_1	4_0	523.2	2.0
	4_{-1}	4_{-2}	568.9	5.9

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	4_{-3}	4_{-4}	80601.0	21.2
	4_{-4}	4_{-3}	607.3	7.3
	4_{-2}	4_{-1}	621.2	2.3
	4_{0}	4_{1}	659.7	0.9
	4_{-1}	4_{2}	676.0	2.7
	4_{-3}	4_{0}	682.7	1.7
	4_{1}	4_{4}	697.6	1.2
R				
	4_{-1}	5_{-4}	621.8	0.5
	4_{0}	5_{-3}	664.9	0.7
	4_{-2}	5_{-1}	746.9	2.9
	4_{-4}	5_{-3}	759.0	2.2
	4_{0}	5_{1}	770.2	2.3
	4_{-3}	5_{-2}	776.3	6.3
	4_{-1}	5_{0}	783.1	7.1
	4_{2}	5_{3}	804.1	1.9
	4_{1}	5_{2}	805.3	5.8
	4_{4}	5_{5}	831.3	1.3
	4_{3}	5_{4}	831.3	4.0
P				
	5_{5}	4_{4}	324.5	1.1
	5_{2}	4_{1}	359.8	0.6
	5_{3}	4_{2}	360.3	1.9
	5_{0}	4_{-1}	391.0	0.9
	5_{1}	4_{0}	396.6	2.9

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_{-2}	4_{-3}	80412.5	0.8
	5_{-1}	4_{-2}	421.9	4.0
	5_{-3}	4_{-4}	425.5	3.0
	5_{-3}	4_{0}	507.1	0.8
	5_{-5}	4_{-2}	543.9	0.5
Q				
	5_{3}	5_{0}	467.4	0.6
	5_{1}	5_{-2}	490.2	0.8
	5_{0}	5_{-1}	516.7	0.5
	5_{-2}	5_{-3}	564.3	1.7
	5_{-4}	5_{-5}	593.8	5.6
	5_{-5}	5_{-4}	596.8	17.3
	5_{-3}	5_{-2}	600.8	5.8
	5_{-1}	5_{0}	636.1	2.2
	5_{-2}	5_{1}	669.6	0.6
	5_{1}	5_{2}	678.8	1.1
R				
	5_{1}	6_{-2}	650.6	0.7
	5_{-1}	6_{-4}	663.9	1.2
	5_{-3}	6_{-2}	761.1	5.1
	5_{-1}	6_{0}	772.8	4.4
	5_{-5}	6_{-4}	785.9	3.9
	5_{-2}	6_{-1}	796.2	1.4
	5_{-4}	6_{-3}	797.8	1.3
	5_{1}	6_{2}	809.0	3.3

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_0	6_1	80813.4	1.1
	5_3	6_4	838.5	2.3
	5_2	6_3	838.8	0.8
	5_5	6_6	863.9	1.3
P				
	6_3	5_2	286.2	0.6
	6_1	5_0	320.8	1.0
	6_{-1}	5_{-2}	349.5	1.4
	6_0	5_{-1}	358.1	0.6
	6_{-3}	5_{-4}	368.3	1.3
	6_{-2}	5_{-3}	375.9	0.7
Q				
	6_{-1}	6_{-2}	509.8	1.0
	6_{-3}	6_{-4}	557.4	3.6
	6_{-4}	6_{-3}	580.1	1.4
	6_{-5}	6_{-6}	584.4	11.6
	6_{-6}	6_{-5}	585.7	3.9
	6_{-3}	6_0	666.3	0.9
	6_{-1}	6_2	668.2	0.8
R				
	6_{-2}	7_{-1}	774.4	0.8
	6_{-4}	7_{-3}	778.0	0.9
	6_0	7_1	808.4	0.6
	6_{-3}	7_{-2}	809.4	2.3
	6_{-6}	7_{-5}	812.1	0.7

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	6_{-5}	7_{-4}	80819.3	2.2
	6_{-1}	7_{0}	819.7	1.8
	6_{1}	7_{2}	843.2	1.2
	6_{3}	7_{4}	868.6	0.7
P				
	7_{-1}	6_{-2}	314.0	0.8
	7_{-3}	6_{-4}	324.7	0.9
	7_{-5}	6_{-6}	325.3	0.7
Q				
	7_{-4}	7_{-5}	547.6	0.8
	7_{-5}	7_{-4}	560.2	2.4
	7_{-6}	7_{-7}	573.1	2.3
	7_{-7}	7_{-6}	573.6	7.0
	7_{-3}	7_{-2}	576.7	0.8
R				
	7_{-3}	8_{-2}	777.2	1.1
	7_{-5}	8_{-4}	797.6	1.1
	7_{-1}	8_{0}	802.5	0.8
	7_{-7}	8_{-6}	836.3	1.1
	7_{1}	8_{2}	841.4	0.5
Q				
	8_{-5}	8_{-6}	534.6	1.2
	8_{-7}	8_{-8}	560.0	3.7
	8_{-8}	8_{-7}	560.3	1.2
R	8_{-7}	9_{-6}	860.3	0.5

APPX III

TABLE III.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
Q				
	9_{-7}	9_{-6}	80521.9	0.6
	9_{-8}	9_{-9}	545.4	0.6
	9_{-9}	9_{-8}	545.5	1.8
Q	10_{-9}	10_{-10}	529.3	0.8

APPX III

TABLE III.2

$\tilde{D}^1A_1$ Transitions in H_2O Calculated for $\langle \mu_z \rangle = 1$

(NO Electronic Interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R	0_0	1_0	82097.5	3.3
P	1_0	0_0	2021.5	2.8
Q				
	1_1	1_{-1}	2037.5	12.2
	1_{-1}	1_1	2078.0	13.3
R				
	1_0	2_{-2}	2084.6	1.9
	1_{-1}	2_{-1}	2111.8	13.3
	1_1	2_1	2158.8	12.2
	1_0	2_2	2164.7	3.7
P				
	2_2	1_0	1960.9	2.1
	2_1	1_1	1966.5	7.7
	2_{-1}	1_{-1}	2000.4	10.2
	2_{-2}	1_0	2027.3	1.8
Q				
	2_1	2_{-1}	2000.3	4.3
	2_2	2_0	2012.0	2.1
	2_0	2_{-2}	2026.5	4.6
	2_{-2}	2_0	2078.4	4.9
	2_0	2_2	2106.6	2.3
	2_{-1}	2_1	2121.6	5.6
R				
	2_1	3_{-1}	2082.9	1.3

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included in this table.

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	2_{-1}	3_{-3}	82103.2	10.3
	2_{-2}	3_{-2}	2122.4	5.1
	2_0	3_0	2169.6	3.5
	2_{-1}	3_1	2188.7	7.7
	2_2	3_2	2227.1	4.1
	2_1	3_3	2228.5	12.4
P				
	3_3	2_1	1913.7	5.8
	3_2	2_{-1}	1914.5	2.0
	3_1	2_{-1}	1923.1	3.3
	3_0	2_0	1941.8	2.0
	3_{-2}	2_{-2}	1979.3	3.5
	3_{-3}	2_{-1}	1998.7	8.9
	3_{-1}	2_1	2027.6	1.3
Q				
	3_2	3_0	1977.6	0.8
	3_3	3_1	1980.7	2.7
	3_0	3_{-2}	1985.8	1.6
	3_1	3_{-1}	2005.7	9.3
	3_{-1}	3_{-3}	2009.2	11.0
	3_{-3}	3_{-1}	2081.3	11.1
	3_{-1}	3_1	2094.7	9.2
	3_{-2}	3_0	2122.5	2.1
	3_1	3_3	2151.2	3.5
	3_0	3_2	2157.0	1.2

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R				
	3_0	4_{-2}	82103.4	0.8
	3_{-2}	4_{-4}	2119.2	4.2
	3_{-3}	4_{-3}	2130.8	15.2
	3_{-1}	4_{-1}	2175.7	8.4
	3_{-2}	4_0	2216.4	1.5
	3_1	4_1	2237.3	8.3
	3_0	4_2	2243.6	2.8
	3_3	4_3	2299.1	8.3
	3_2	4_4	2299.3	2.8
P				
	4_4	3_2	1869.0	1.0
	4_3	3_3	1869.1	3.0
	4_2	3_0	1879.0	1.1
	4_1	3_1	1883.7	3.6
	4_{-1}	3_{-1}	1917.3	4.4
	4_{-3}	3_{-3}	1957.7	9.6
	4_{-4}	3_{-2}	1970.1	3.2
	4_{-2}	3_0	1988.8	0.7
	4_{-3}	3_1	2043.2	0.8
Q				
	4_3	4_1	1955.2	1.0
	4_1	4_{-1}	1964.7	2.9
	4_{-1}	4_{-3}	1966.8	3.9
	4_2	4_0	1972.9	1.1
	4_{-2}	4_{-4}	1985.6	2.2

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'} \times 10$
	4_0	4_{-2}	81993.7	2.8
	4_{-2}	4_0	2082.7	2.6
	4_{-4}	4_{-2}	2087.8	2.2
	4_{-3}	4_{-1}	2124.2	5.2
	4_0	4_2	2133.9	1.3
	4_{-1}	4_1	2148.9	3.9
	4_2	4_4	2200.7	0.5
	4_1	4_3	2202.0	1.5
R				
	4_1	5_{-1}	2089.3	0.5
	4_{-1}	5_{-3}	2122.3	2.8
	4_{-3}	5_{-5}	2132.2	12.0
	4_{-4}	5_{-4}	2138.3	4.4
	4_{-2}	5_{-2}	2177.9	2.1
	4_0	5_0	2241.3	1.7
	4_{-3}	5_{-1}	2248.7	2.2
	4_{-1}	5_1	2258.8	5.1
	4_2	5_2	2308.4	1.7
	4_1	5_3	2309.8	5.1
	4_4	5_4	2375.4	1.3
	4_3	5_5	2375.4	3.9
P				
	5_5	4_3	1828.9	1.1
	5_3	4_1	1833.2	1.6
	5_2	4_2	1834.0	0.5

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_1	4_{-1}	81838.2	1.5
	5_0	4_0	1852.5	0.7
	5_{-2}	4_{-2}	1893.0	1.0
	5_{-4}	4_{-4}	1934.5	2.6
	5_{-5}	4_{-3}	1941.8	7.9
	5_{-3}	4_{-1}	1948.7	2.3
	5_{-1}	4_1	2001.9	0.5
Q				
	5_3	5_1	1943.1	1.0
	5_{-2}	5_{-4}	1943.6	0.8
	5_0	5_{-2}	1947.7	0.7
	5_{-3}	5_{-5}	1956.7	3.5
	5_1	5_{-1}	1962.7	3.1
	5_{-1}	5_{-3}	1975.3	5.7
	5_{-3}	5_{-1}	2073.2	5.0
	5_{-5}	5_{-3}	2097.3	3.6
	5_{-1}	5_1	2111.8	2.8
	5_{-4}	5_{-2}	2126.8	1.1
	5_{-2}	5_0	2140.7	1.0
	5_1	5_3	2183.2	1.5
	5_0	5_2	2188.1	0.5
	5_3	5_5	2253.4	0.5
R				
	5_{-2}	6_{-4}	2139.0	0.9
	5_{-4}	6_{-6}	2142.4	3.2

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_{-5}	6_{-5}	82145.4	9.8
	5_{-3}	6_{-3}	2177.7	4.3
	5_{-1}	6_{-1}	2239.4	2.7
	5_{-2}	6_{0}	2275.7	0.9
	5_{1}	6_{1}	2312.9	2.7
	5_{0}	6_{2}	2318.1	0.9
	5_{-5}	6_{-1}	2361.5	0.5
	5_{3}	6_{3}	2382.6	2.1
	5_{2}	6_{4}	2382.8	0.7
	5_{5}	6_{5}	2456.4	1.3
P				
	6_{3}	5_{3}	1790.7	0.5
	6_{1}	5_{1}	1796.5	0.8
	6_{-1}	5_{-1}	1821.9	1.0
	6_{-3}	5_{-3}	1868.8	1.9
	6_{-4}	5_{-2}	1909.0	0.6
	6_{-5}	5_{-5}	1909.2	5.3
	6_{-6}	5_{-4}	1913.1	1.8
Q				
	6_{-3}	6_{-5}	1916.9	1.4
	6_{1}	6_{-1}	1924.2	0.7
	6_{-4}	6_{-6}	1924.7	0.5
	6_{-1}	6_{-3}	1926.4	1.4
	6_{0}	6_{-2}	1948.3	0.7
	6_{-2}	6_{-4}	1950.6	1.0

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	6_{-4}	6_{-2}	82068.3	0.8
	6_{-2}	6_{0}	2087.3	0.6
	6_{-6}	6_{-4}	2108.5	0.6
	6_{-5}	6_{-3}	2130.2	1.9
	6_{-3}	6_{-1}	2132.9	1.8
	6_{-1}	6_{1}	2172.2	1.0
R				
	6_{-5}	7_{-7}	2150.2	6.4
	6_{-6}	7_{-6}	2151.6	2.2
	6_{-3}	7_{-5}	2152.6	2.0
	6_{-4}	7_{-4}	2176.9	0.9
	6_{-2}	7_{-2}	2232.8	0.5
	6_{-3}	7_{-1}	2296.3	1.1
	6_{-1}	7_{1}	2325.0	1.3
	6_{1}	7_{3}	2387.2	1.0
	6_{3}	7_{5}	2461.1	0.6
P				
	7_{-5}	6_{-3}	1871.1	1.2
	7_{-6}	6_{-6}	1881.7	1.1
	7_{-7}	6_{-5}	1883.7	3.3
Q				
	7_{-5}	7_{-7}	1891.2	0.7
	7_{1}	7_{-1}	1912.1	0.5
	7_{-3}	7_{-5}	1919.9	1.2
	7_{-1}	7_{-3}	1928.1	1.1

APPX III

TABLE III.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	7_{-3}	7_{-1}	82063.7	0.9
	7_{-5}	7_{-3}	2068.6	1.0
	7_{-7}	7_{-5}	2119.4	0.9
R				
	7_{-6}	8_{-8}	2156.0	1.3
	7_{-7}	8_{-7}	2156.6	3.8
	7_{-5}	8_{-5}	2176.6	1.5
	7_{-3}	8_{-3}	2223.2	0.7
	7_{-1}	8_{-1}	2302.3	0.5
P				
	8_{-5}	7_{-5}	1817.7	0.6
	8_{-7}	7_{-7}	1852.1	1.8
	8_{-8}	7_{-6}	1853.0	0.6
Q	8_{-7}	8_{-5}	2137.5	0.5
R				
	8_{-7}	9_{-9}	2159.9	2.0
	8_{-8}	9_{-8}	2160.2	0.7
	8_{-5}	9_{-7}	2169.5	0.7
P	9_{-9}	8_{-7}	1821.0	0.9
R	9_{-9}	10_{-9}	2162.2	0.9

APPENDIX III

TABLE III.3

$\tilde{C}^1B_1$ Transitions in D_2O Calculated for $\langle\mu_x\rangle = 1$.
(No electronic interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R	0_0	1_1	80772.8	6.7
P	1_1	0_0	729.2	3.0
Q				
	1_0	1_{-1}	742.4	9.1
	1_{-1}	1_0	758.8	4.7
R				
	1_1	2_{-2}	761.2	1.1
	1_{-1}	2_0	784.1	4.7
	1_1	2_2	798.8	4.9
	1_0	2_1	801.0	9.1
P				
	2_1	1_0	697.3	3.5
	2_2	1_1	698.7	7.8
	2_0	1_{-1}	713.3	7.8
	2_{-2}	1_1	737.0	1.8
Q				
	2_2	2_{-1}	716.4	2.5
	2_1	2_0	722.6	1.9
	2_{-1}	2_{-2}	741.8	7.4
	2_{-2}	2_{-1}	754.6	15.6
	2_0	2_1	771.9	4.4
	2_{-1}	2_2	779.4	1.6

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included in this table.

APPX III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R				
	2_2	3_{-1}	80756.6	1.1
	2_0	3_{-3}	765.6	2.9
	2_{-2}	3_{-1}	795.1	10.5
	2_0	3_1	805.5	11.1
	2_{-1}	3_0	811.3	4.5
	2_2	3_3	825.8	11.8
	2_1	3_2	826.3	5.9
P				
	3_2	2_1	664.3	7.9
	3_3	2_2	664.6	4.0
	3_0	2_{-1}	680.5	6.5
	3_1	2_0	684.0	4.2
	3_{-1}	2_{-2}	694.8	4.1
	3_{-3}	2_0	725.7	1.1
	3_{-2}	2_1	746.7	0.5
Q				
	3_3	3_0	696.5	1.1
	3_2	3_1	697.9	2.3
	3_1	3_{-2}	707.5	1.2
	3_0	3_{-1}	721.0	6.1
	3_{-2}	3_{-3}	740.4	19.8
	3_{-3}	3_{-2}	749.2	10.5
	3_{-1}	3_0	764.4	3.5

APPX III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R	3_{-2}	3_1	80780.3	3.6
	3_1	3_2	787.7	1.5
	3_0	3_3	789.9	2.9
	3_0	4_{-3}	748.4	0.8
	3_1	4_{-2}	764.8	1.2
	3_{-1}	4_{-4}	766.3	1.3
	3_{-3}	4_{-2}	806.6	4.8
	3_{-1}	4_0	811.0	5.8
	3_{-2}	4_{-1}	821.6	8.4
	3_1	4_2	831.3	5.4
	3_0	4_1	833.3	10.8
	3_2	4_3	851.0	11.0
	3_3	4_4	850.9	5.5
P	4_3	3_2	629.2	3.2
	4_4	3_3	629.3	6.3
	4_1	3_0	647.2	3.4
	4_2	3_1	648.2	7.0
	4_{-1}	3_{-2}	661.6	2.8
	4_0	3_{-1}	666.8	8.6
	4_{-2}	3_{-3}	673.7	7.2
	4_{-2}	3_1	713.6	1.4
	4_{-4}	3_{-1}	715.9	1.7

APPX III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
Q				
	4_4	4_1	80672.7	1.4
	4_3	4_2	672.8	0.7
	4_2	4_{-1}	689.6	2.8
	4_1	4_0	693.9	1.6
	4_0	4_{-3}	694.1	1.4
	4_{-1}	4_{-2}	719.0	3.7
	4_{-3}	4_{-4}	737.9	11.5
	4_{-4}	4_{-3}	743.3	24.0
	4_{-2}	4_{-1}	754.9	8.5
	4_0	4_1	779.1	4.1
	4_{-3}	4_0	782.6	1.4
	4_{-1}	4_2	785.4	2.0
	4_2	4_3	801.3	1.9
	4_1	4_4	801.7	1.0
R				
	4_{-1}	5_{-4}	748.2	0.5
	4_2	5_{-1}	750.9	0.9
	4_{-2}	5_{-5}	763.3	1.8
	4_0	5_{-3}	769.7	3.0
	4_{-2}	5_{-1}	816.3	11.0
	4_{-4}	5_{-3}	818.8	7.8
	4_{-3}	5_{-2}	831.7	3.6
	4_0	5_1	834.2	9.4
	4_{-1}	5_0	839.6	4.7

APPX III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	4_2	5_3	80855.6	9.1
	4_1	5_2	856.0	4.6
	4_4	5_5	874.3	8.0
	4_3	5_4	874.3	4.0
P				
	5_4	4_3	592.6	4.0
	5_5	4_4	592.6	2.0
	5_2	4_1	611.0	5.0
	5_3	4_2	611.2	2.5
	5_0	4_{-1}	628.3	5.6
	5_1	4_0	630.7	3.0
	5_{-2}	4_{-3}	640.7	4.5
	5_{-1}	4_{-2}	646.9	3.8
	5_{-3}	4_{-4}	650.1	2.7
	5_{-3}	4_0	694.8	0.8
	5_{-5}	4_{-2}	707.8	0.6
	5_{-2}	4_1	725.7	0.5
	5_{-4}	4_{-1}	725.7	0.7
Q				
	5_4	5_3	646.9	0.7
	5_3	5_0	665.4	0.9
	5_2	5_1	666.1	1.8
	5_1	5_{-2}	679.8	1.1
	5_0	5_{-1}	689.6	3.3
	5_{-2}	5_{-3}	716.2	8.0

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_{-4}	5_{-5}	80734.1	23.5
	5_{-5}	5_{-4}	737.1	12.1
	5_{-3}	5_{-2}	743.9	4.6
	5_{-1}	5_{0}	767.5	2.1
	5_{-2}	5_{1}	780.8	3.8
	5_{-4}	5_{-1}	787.1	1.7
	5_{1}	5_{2}	792.8	1.3
	5_{0}	5_{3}	794.3	2.6
	5_{3}	5_{4}	812.6	0.5
	5_{2}	5_{5}	812.7	1.1
R				
	5_{0}	6_{-3}	744.4	0.8
	5_{-2}	6_{-5}	745.7	0.8
	5_{-3}	6_{-6}	757.2	0.6
	5_{1}	6_{-2}	757.6	0.7
	5_{-1}	6_{-4}	770.7	1.4
	5_{-3}	6_{-2}	821.8	4.5
	5_{-5}	6_{-4}	831.7	2.9
	5_{-1}	6_{0}	834.9	3.9
	5_{-4}	6_{-3}	841.8	5.8
	5_{-2}	6_{-1}	845.3	7.6
	5_{1}	6_{2}	858.2	3.6
	5_{0}	6_{1}	859.6	7.2
	5_{3}	6_{4}	877.7	3.1

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	5_2	6_3	80877.8	6.2
	5_5	6_6	896.2	2.4
	5_4	6_5	896.2	4.8
P				
	6_5	5_4	554.4	1.0
	6_6	5_5	554.4	2.0
	6_3	5_2	573.0	1.4
	6_4	5_3	573.0	2.9
	6_1	5_0	591.2	1.9
	6_2	5_1	591.7	3.8
	6_{-1}	5_{-2}	607.3	2.1
	6_0	5_{-1}	611.5	5.0
	6_{-3}	5_{-4}	617.9	1.7
	6_{-2}	5_{-3}	624.1	5.9
	6_{-4}	5_{-5}	624.5	3.8
	6_{-4}	5_{-1}	677.4	1.3
	6_{-2}	5_1	688.7	0.6
	6_{-6}	5_{-3}	701.1	0.7
Q				
	6_4	6_1	638.3	0.9
	6_2	6_{-1}	656.2	1.6
	6_1	6_0	658.6	0.8
	6_0	6_{-3}	666.2	1.4
	6_{-1}	6_{-2}	685.1	1.5
	6_{-3}	6_{-4}	712.5	4.0
	6_{-5}	6_{-6}	729.0	10.8

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	6_{-6}	6_{-5}	80730.5	21.9
	6_{-4}	6_{-3}	732.2	9.0
	6_{-2}	6_{-1}	753.2	3.8
	6_{-3}	6_{0}	776.8	1.4
	6_{0}	6_{1}	781.5	2.4
	6_{-1}	6_{2}	785.7	1.2
	6_{-5}	6_{-2}	793.6	0.5
	6_{2}	6_{3}	803.3	1.4
	6_{1}	6_{4}	803.5	0.7
	6_{4}	6_{5}	822.3	0.5
R				
	6_{2}	7_{-1}	737.2	0.5
	6_{-4}	7_{-7}	748.9	0.8
	6_{0}	7_{-3}	762.3	1.5
	6_{-2}	7_{-5}	767.6	2.1
	6_{-4}	7_{-3}	828.2	6.5
	6_{-2}	7_{-1}	834.2	6.2
	6_{-6}	7_{-5}	844.6	4.3
	6_{-3}	7_{-2}	850.8	2.8
	6_{-5}	7_{-4}	851.8	2.2
	6_{0}	7_{1}	858.2	5.2
	6_{-1}	7_{0}	862.0	2.7
	6_{2}	7_{3}	879.4	4.5
	6_{1}	7_{2}	879.7	2.3
	6_{4}	7_{5}	898.2	3.5

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	6_3	7_4	80898.2	1.7
	6_6	7_7	916.6	2.4
	6_5	7_6	916.6	1.2
P				
	7_6	6_5	514.8	0.9
	7_4	6_3	533.4	1.4
	7_5	6_4	533.4	0.7
	7_2	6_1	551.8	2.0
	7_3	6_2	551.8	1.0
	7_0	6_{-1}	569.5	2.7
	7_1	6_0	570.8	1.4
	7_{-2}	6_{-3}	584.3	3.0
	7_{-1}	6_{-2}	589.9	1.9
	7_{-4}	6_{-5}	593.5	2.3
	7_{-5}	6_{-6}	597.6	1.3
	7_{-3}	6_{-4}	598.6	2.0
Q				
	7_2	7_1	628.6	0.8
	7_1	7_{-2}	644.8	0.6
	7_0	7_{-1}	650.6	1.3
	7_{-2}	7_{-3}	680.3	2.6
	7_{-4}	7_{-5}	707.6	7.2
	7_{-5}	7_{-4}	720.4	4.0
	7_{-6}	7_{-7}	722.7	18.1
	7_{-7}	7_{-6}	723.5	9.1
	7_{-3}	7_{-2}	736.9	1.6

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	7_{-1}	7_0	766.8	1.0
	7_{-4}	7_{-1}	774.3	1.8
	7_{-2}	7_1	776.3	2.0
	7_1	7_2	791.9	0.6
	7_0	7_3	792.8	1.3
	7_{-6}	7_{-3}	802.0	0.5
	7_2	7_5	811.7	0.6
R				
	7_{-2}	8_{-5}	739.8	0.6
	7_{-3}	8_{-6}	760.5	0.6
	7_{-1}	8_{-4}	763.7	0.7
	7_{-3}	8_{-2}	833.2	2.2
	7_{-5}	8_{-4}	835.9	2.1
	7_{-1}	8_0	855.4	1.8
	7_{-4}	8_{-3}	856.2	4.0
	7_{-7}	8_{-6}	856.9	1.5
	7_{-6}	8_{-5}	861.5	3.1
	7_{-2}	8_{-1}	863.5	3.8
	7_1	8_2	879.2	1.5
	7_0	8_1	880.0	3.1
	7_3	8_4	898.6	1.2
	7_2	8_3	898.6	2.3
	7_5	8_6	917.2	0.8
	7_4	8_5	917.2	1.6
	7_7	8_8	935.6	0.5

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	7_6	8_7	80935.6	1.0
P				
	8_6	7_5	492.3	0.6
	8_4	7_3	510.8	0.9
	8_1	7_0	529.0	0.7
	8_2	7_1	529.2	1.3
	8_{-1}	7_{-2}	546.1	0.9
	8_0	7_{-1}	548.5	1.9
	8_{-3}	7_{-4}	559.3	1.0
	8_{-2}	7_{-3}	565.5	2.6
	8_{-5}	7_{-6}	567.8	0.8
	8_{-6}	7_{-7}	570.0	1.6
	8_{-4}	7_{-5}	570.6	2.5
	8_{-4}	7_{-1}	637.3	0.5
	8_{-6}	7_{-3}	649.3	0.5
Q				
	8_2	8_{-1}	616.4	0.5
	8_0	8_{-3}	630.4	0.7
	8_{-1}	8_{-2}	642.4	0.5
	8_{-3}	8_{-4}	674.9	1.0
	8_{-5}	8_{-6}	701.2	3.0
	8_{-6}	8_{-5}	708.8	6.4
	8_{-7}	8_{-8}	715.4	7.0
	8_{-8}	8_{-7}	715.7	14.2

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	8_{-4}	8_{-3}	719.2	2.6
	8_{-2}	8_{-1}	748.8	1.4
	8_{-3}	8_{0}	766.6	0.7
	8_{-5}	8_{-2}	773.9	0.5
	8_{0}	8_{1}	777.9	0.9
	8_{-1}	8_{2}	780.4	0.5
	8_{2}	8_{3}	799.3	0.5
R				
	8_{0}	9_{-3}	744.0	0.5
	8_{-4}	9_{-7}	750.0	0.7
	8_{-2}	9_{-5}	761.1	1.1
	8_{-4}	9_{-3}	832.8	2.9
	8_{-6}	9_{-5}	844.9	2.6
	8_{-2}	9_{-1}	850.0	2.3
	8_{-5}	9_{-4}	861.5	1.3
	8_{-3}	9_{-2}	864.4	1.2
	8_{-8}	9_{-7}	868.1	2.1
	8_{-7}	9_{-6}	870.9	1.0
	8_{0}	9_{1}	876.5	1.9
	8_{-1}	9_{0}	878.8	1.0
	8_{2}	9_{3}	897.3	1.5
	8_{1}	9_{2}	897.4	0.7
	8_{4}	9_{5}	916.2	1.0
	8_{3}	9_{4}	916.2	0.5

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	8_6	9_7	80934.7	0.6
P				
	9_2	8_1	486.6	0.5
	9_0	8_{-1}	504.5	0.8
	9_{-2}	8_{-3}	520.7	1.1
	9_{-1}	8_{-2}	524.5	0.6
	9_{-4}	8_{-5}	532.6	1.2
	9_{-3}	8_{-4}	538.3	0.8
	9_{-5}	8_{-6}	540.7	0.7
	9_{-6}	8_{-7}	540.8	0.9
	9_{-7}	8_{-8}	541.9	0.5
Q				
	9_{-2}	9_{-3}	634.3	0.6
	9_{-4}	9_{-5}	668.7	1.6
	9_{-6}	9_{-7}	693.2	4.5
	9_{-7}	9_{-6}	697.4	2.3
	9_{-5}	9_{-4}	701.1	1.0
	9_{-8}	9_{-9}	701.1	10.2
	9_{-9}	9_{-8}	707.3	5.1
	9_{-3}	9_{-2}	727.8	0.5
	9_{-4}	9_{-1}	757.5	0.8
	9_{-2}	9_1	766.8	0.7
	9_{-6}	9_{-3}	775.9	0.5
R				
	9_{-5}	10_{-4}	833.8	0.9

APPX. III

TABLE III.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	9_{-3}	10_{-2}	80842.8	0.7
	9_{-7}	10_{-6}	854.4	0.8
	9_{-4}	10_{-3}	864.9	1.5
	9_{-6}	10_{-5}	866.9	1.6
	9_{-1}	10_{0}	871.0	0.6
	9_{-2}	10_{-1}	876.4	1.2
	9_{-9}	10_{-8}	878.2	0.7
	9_{-8}	10_{-7}	879.7	1.3
	9_{0}	10_{1}	894.5	0.9
	9_{2}	10_{3}	913.5	0.6
P				
	10_{0}	9_{-1}	479.3	0.5
	10_{-2}	9_{-3}	498.1	0.8
	10_{-4}	9_{-5}	508.4	0.9
	10_{-6}	9_{-7}	509.5	0.8
	10_{-8}	9_{-9}	513.3	0.6
Q				
	10_{-5}	10_{-6}	661.2	0.6
	10_{-6}	10_{-5}	683.3	1.4
	10_{-7}	10_{-8}	683.7	1.5
	10_{-8}	10_{-7}	685.9	3.2
	10_{-9}	10_{-10}	697.9	3.5
	10_{-10}	10_{-9}	698.0	7.0
	10_{-4}	10_{-3}	704.7	0.6

APPX. III

TABLE III.3 (Continued)

INDENTIFICATION		FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$ $J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R			
	10_{-4} 11_{-3}	80835.3	0.8
	$10_{-6}11_{-5}$	836.7	0.9
	$10_{-2}11_{-1}$	862.3	0.6
	$10_{-8}11_{-7}$	863.6	0.9
	$10_{-7}11_{-6}$	972.2	0.5
	$10_{-10}11_{-9}$	887.1	0.8
	10_{0} 11_{1}	888.6	0.5

APPX. III TABLE III.4

$\tilde{D}^1A_1$ Transitions in D_2O Calculated for $\langle\mu_z\rangle = 1$

(No Electronic Interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
R	0_0	1_0	82095.3	6.7
P	1_0	0_0	2054.7	6.0
Q				
	1_1	1_{-1}	2063.0	4.5
	1_{-1}	1_1	2085.2	4.7
R				
	1_0	2_{-2}	2086.6	3.9
	1_{-1}	2_{-1}	2102.7	4.7
	1_1	2_1	2127.2	4.5
	1_0	2_2	2129.9	8.2
P				
	2_2	1_0	2021.2	6.0
	2_1	1_1	2023.7	3.5
	2_{-1}	1_{-1}	2043.6	4.1
	2_{-2}	1_0	2059.4	3.9
Q				
	2_1	2_{-1}	2041.2	1.9
	2_2	2_0	2046.7	5.4
	2_0	2_{-2}	2057.5	11.8
	2_{-2}	2_0	2084.9	12.1
	2_0	2_2	2100.8	5.6
	2_{-1}	2_1	2107.8	2.3

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included in this table.

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
R				
	2_2	3_{-2}	82069.8	0.5
	2_1	3_{-1}	2082.1	0.5
	2_{-1}	3_{-3}	2095.9	3.9
	2_{-2}	3_{-2}	2108.0	11.9
	2_0	3_0	2132.8	8.7
	2_{-1}	3_1	2141.4	3.3
	2_2	3_2	2161.6	11.3
	2_1	3_3	2162.1	5.6
P				
	3_3	2_1	1993.0	3.7
	3_2	2_2	1993.3	7.5
	3_1	2_{-1}	2002.6	2.0
	3_0	2_0	2010.8	6.5
	3_{-2}	2_{-2}	2032.3	9.7
	3_{-3}	2_{-1}	2044.3	3.8
	3_{-1}	2_1	2060.9	0.6
	3_{-2}	2_2	2075.6	0.7
Q				
	3_2	3_0	2025.2	3.1
	3_3	3_1	2026.5	1.6
	3_0	3_{-2}	2033.9	5.3
	3_1	3_{-1}	2043.5	4.7
	3_{-1}	3_{-3}	2049.0	5.8
	3_{-3}	3_{-1}	2085.3	5.7

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	3_{-1}	3_1	82094.4	4.5
	3_{-2}	3_0	2107.6	6.1
	3_1	3_3	2123.5	1.9
	3_0	3_2	2125.7	3.8
R				
	3_0	4_{-2}	2092.0	2.3
	3_{-2}	4_{-4}	2104.0	11.2
	3_{-3}	4_{-3}	2111.9	6.9
	3_{-1}	4_{-1}	2135.8	4.2
	3_{-2}	4_0	2154.1	4.6
	3_1	4_1	2166.9	4.6
	3_0	4_2	2169.3	9.3
	3_3	4_3	2196.7	5.3
	3_2	4_4	2196.7	10.6
P				
	4_4	3_2	1965.0	6.0
	4_3	3_3	1965.1	3.0
	4_2	3_0	1975.6	5.5
	4_1	3_1	1977.3	2.9
	4_0	3_{-2}	1979.7	2.2
	4_{-1}	3_{-1}	1997.6	2.0
	4_{-3}	3_{-3}	2020.6	5.3
	4_{-4}	3_{-2}	2028.8	10.1
	4_{-2}	3_0	2040.9	2.4

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10
	4_{-3}	3_1	82066.0	0.5
	4_0	3_2	2071.5	0.5
Q				
	4_3	4_1	2008.5	0.9
	4_4	4_2	2008.6	1.9
	4_1	4_{-1}	2018.7	2.3
	4_2	4_0	2022.1	5.0
	4_{-1}	4_{-3}	2024.3	2.7
	4_{-2}	4_{-4}	2037.3	9.4
	4_0	4_{-2}	2037.8	11.3
	4_{-4}	4_{-2}	2086.9	8.8
	4_{-2}	4_0	2087.4	10.3
	4_{-3}	4_{-1}	2107.5	3.1
	4_0	4_2	2115.1	5.2
	4_{-1}	4_1	2121.0	2.6
	4_2	4_4	2147.1	2.4
	4_1	4_3	2147.4	1.2
R				
	4_2	5_{-2}	2071.4	0.5
	4_{-1}	5_{-3}	2101.1	1.7
	4_{-3}	5_{-5}	2110.4	6.5
	4_{-4}	5_{-4}	2115.1	14.5
	4_{-2}	5_{-2}	2136.7	7.8

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10
	4_{-3}	5_{-1}	82168.6	1.4
	4_0	5_0	2169.3	7.2
	4_{-1}	5_1	2176.1	3.6
	4_2	5_2	2201.3	8.2
	4_1	5_3	2201.7	4.1
	4_{-4}	5_0	2218.4	0.5
	4_4	5_4	2232.9	7.8
	4_3	5_5	2232.9	3.9
P				
	5_5	4_3	1938.3	1.9
	5_4	4_4	1938.3	3.8
	5_3	4_1	1946.8	2.2
	5_2	4_2	1947.0	4.4
	5_{-1}	4_{-3}	1952.2	0.5
	5_1	4_{-1}	1955.5	1.8
	5_0	4_0	1960.8	4.3
	5_{-2}	4_{-2}	1984.3	5.2
	5_{-4}	4_{-4}	2008.1	10.7
	5_{-5}	4_{-3}	2013.2	5.4
	5_{-3}	4_{-1}	2019.6	1.7
	5_{-4}	4_0	2058.2	0.8
	5_{-2}	4_2	2061.6	0.8
Q				
	5_4	5_2	1992.6	0.9

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TABLE III.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY
Branch $J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	5_5 5_3	81992.6	0.5
	5_2 5_0	2001.2	2.6
	5_3 5_1	2001.8	1.3
	5_0 5_{-2}	2010.1	4.7
	5_{-2} 5_{-4}	2012.5	4.6
	5_1 5_{-1}	2016.7	3.0
	5_{-3} 5_{-5}	2022.6	3.4
	5_{-1} 5_{-3}	2029.0	5.4
	5_{-3} 5_{-1}	2080.8	4.7
	5_{-5} 5_{-3}	2090.0	3.1
	5_{-1} 5_1	2104.0	2.7
	5_{-4} 5_{-2}	2107.5	5.3
	5_{-2} 5_0	2115.9	5.3
	5_1 5_3	2138.3	1.6
	5_0 5_2	2140.0	3.2
	5_3 5_5	2171.2	0.7
	5_2 5_4	2171.2	1.3
R			
	5_0 6_{-2}	2087.8	1.0
	5_{-2} 6_{-4}	2109.0	4.1
	5_{-4} 6_{-6}	2115.3	13.2
	5_{-5} 6_{-5}	2117.9	6.9

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10
	5_{-3}	6_{-3}	82135.9	3.5
	5_{-1}	6_{-1}	2168.7	2.7
	5_{-4}	6_{-2}	2185.3	1.7
	5_{-2}	6_{0}	2183.0	5.1
	5_{1}	6_{1}	2203.9	3.0
	5_{0}	6_{2}	2205.4	6.1
	5_{3}	6_{3}	2236.3	2.9
	5_{2}	6_{4}	2236.3	5.7
	5_{5}	6_{5}	2270.4	2.4
	5_{4}	6_{6}	2270.4	4.7
P				
	6_{4}	5_{2}	1918.7	2.6
	6_{3}	5_{3}	1918.7	1.3
	6_{6}	5_{4}	1913.0	2.0
	6_{5}	5_{5}	1913.0	1.0
	6_{2}	5_{0}	1926.7	2.9
	6_{1}	5_{1}	1927.6	1.5
	6_{0}	5_{-2}	1931.9	2.1
	6_{-1}	5_{-1}	1944.2	1.6
	6_{-3}	5_{-3}	1970.8	2.2
	6_{-5}	5_{-5}	1994.4	5.0
	6_{-6}	5_{-4}	1997.4	10.2
	6_{-4}	5_{-2}	1997.9	3.8

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TABLE III.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	6_{-2}	5_0	82023.7	1.1
	6_{-3}	5_1	2045.8	0.5
Q				
	6_3	6_1	1984.0	0.6
	6_4	6_2	1984.1	1.2
	6_1	6_{-1}	1992.3	1.3
	6_2	6_0	1993.9	2.8
	6_{-3}	6_{-5}	1998.7	1.8
	6_{-1}	6_{-3}	1999.3	2.1
	6_{-4}	6_{-6}	2005.7	4.4
	6_0	6_{-2}	2009.7	6.0
	6_{-2}	6_{-4}	2016.9	8.5
	6_{-4}	6_{-2}	2075.6	7.0
	6_{-2}	6_0	2090.9	4.9
	6_{-6}	6_{-4}	2093.9	4.2
	6_{-5}	6_{-3}	2107.7	2.0
	6_{-3}	6_{-1}	2110.5	2.2
	6_0	6_2	2127.3	3.0
	6_{-1}	6_1	2131.3	1.6
	6_2	6_4	2161.8	1.7
	6_1	6_3	2162.1	0.8
	6_4	6_6	2196.5	0.6
R				
	6_{-1}	7_{-3}	2095.4	0.6

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$ $J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	6_{-3} 7_{-5}	82115.5	2.2
	6_{-5} 7_{-7}	2118.8	6.0
	6_{-6} 7_{-6}	2120.1	12.2
	6_{-4} 7_{-4}	2134.2	6.1
	6_{-2} 7_{-2}	2165.3	3.9
	6_{-3} 7_{-1}	2191.1	1.6
	6_{0} 7_{0}	2203.6	4.1
	6_{-5} 7_{-3}	2203.9	0.5
	6_{-1} 7_{1}	2208.0	2.1
	6_{-6} 7_{-2}	2242.3	0.5
	6_{2} 7_{2}	2238.0	4.0
	6_{1} 7_{3}	2238.2	2.0
	6_{4} 7_{4}	2272.4	3.3
	6_{3} 7_{5}	2272.4	1.6
	6_{5} 7_{7}	2309.3	1.2
	6_{6} 7_{6}	2309.3	2.4
P			
	7_{6} 6_{6}	1889.0	0.9
	7_{5} 6_{3}	1891.9	0.6
	7_{4} 6_{4}	1891.9	1.3
	7_{3} 6_{1}	1897.5	0.8
	7_{2} 6_{2}	1897.6	1.7
	7_{-1} 6_{-3}	1904.0	0.5

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$ $J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	7_1 6_{-1}	81904.5	0.9
	7_0 6_0	1907.2	1.9
	7_{-2} 6_{-2}	1927.7	2.1
	7_{-4} 6_{-4}	1956.9	3.7
	7_{-5} 6_{-3}	1976.3	1.8
	7_{-6} 6_{-6}	1979.5	8.5
	7_{-7} 6_{-5}	1981.1	4.3
	7_{-3} 6_{-1}	1996.6	0.6
	7_{-4} 6_0	2030.9	0.8
	7_{-2} 6_2	2045.3	0.5
Q			
	7_4 7_2	1968.0	0.5
	7_2 7_{-6}	1973.9	1.2
	7_3 7_1	1974.2	0.6
	7_0 7_{-2}	1981.6	2.3
	7_{-4} 7_{-6}	1983.1	2.5
	7_1 7_{-1}	1985.0	1.3
	7_{-2} 7_2	1986.2	3.2
	7_{-5} 7_{-7}	1987.4	1.4
	7_{-1} 7_{-3}	2000.1	2.6
	7_{-3} 7_{-5}	2001.6	2.9
	7_{-5} 7_{-3}	2072.4	2.2
	7_{-3} 7_{-1}	2077.1	1.9

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	$[I]^{J''}_{J'}$ x 10
	7_{-7}	7_{-5}	82097.9	1.4
	7_{-4}	7_{-2}	2105.3	3.4
	7_{-6}	7_{-4}	2108.0	2.9
	7_{-1}	7_{1}	2112.8	1.2
	7_{-2}	7_{-6}	2121.7	2.5
	7_{1}	7_{3}	2150.4	0.8
	7_{0}	7_{2}	2151.3	1.5
	7_{2}	7_{6}	2185.9	0.7
R				
	7_{-2}	8_{-4}	2102.3	1.1
	7_{-4}	8_{-6}	2120.3	4.0
	7_{-6}	8_{-8}	2121.1	9.9
	7_{-7}	8_{-7}	2121.7	5.0
	7_{-5}	8_{-5}	2132.1	2.5
	7_{-3}	8_{-3}	2159.7	1.4
	7_{-1}	8_{-1}	2200.1	1.3
	7_{-4}	8_{-2}	2200.9	1.8
	7_{-2}	8_{0}	2210.0	2.7
	7_{-6}	8_{-4}	2224.0	0.5
	7_{1}	8_{1}	2237.6	1.3
	7_{0}	8_{2}	2238.5	2.6
	7_{3}	8_{3}	2272.8	1.1
	7_{2}	8_{4}	2272.8	2.1

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	7_5	8_5	82309.9	0.8
	7_4	8_6	2309.9	1.5
	7_7	8_7	2349.6	0.5
	7_6	8_8	2349.6	1.0
P				
	8_6	7_4	1866.5	0.5
	8_4	7_2	1869.3	0.8
	8_2	7_0	1874.6	1.0
	8_1	7_1	1875.0	0.5
	8_0	7_{-2}	1879.5	1.0
	8_{-1}	7_{-1}	1886.3	0.6
	8_{-3}	7_{-3}	1911.4	0.7
	8_{-5}	7_{-5}	1942.3	1.5
	8_{-6}	7_{-4}	1955.3	3.1
	8_{-7}	7_{-7}	1963.4	3.3
	8_{-8}	7_{-6}	1964.2	6.7
	8_{-4}	7_{-2}	1968.3	1.1
Q				
	8_4	8_2	1956.5	0.5
	8_1	8_{-1}	1962.3	0.5
	8_2	8_0	1962.9	1.0
	8_{-5}	8_{-7}	1966.0	0.8
	8_{-6}	8_{-8}	1968.4	1.7
	8_{-1}	8_{-3}	1968.9	0.9

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10
	8_{-3}	8_{-5}	81971.1	1.1
	8_{0}	8_{-2}	1975.1	2.1
	8_{-4}	8_{-6}	1983.3	3.4
	8_{-2}	8_{-4}	1987.5	3.8
	8_{-4}	8_{-2}	2063.9	2.7
	8_{-6}	8_{-4}	2071.3	2.6
	8_{-2}	8_{0}	2095.3	1.7
	8_{-5}	8_{-3}	2100.4	1.2
	8_{-8}	8_{-6}	2101.4	1.9
	8_{-7}	8_{-5}	2108.1	1.0
	8_{-3}	8_{-1}	2111.4	0.9
	8_{0}	8_{2}	2136.5	1.1
	8_{-1}	8_{1}	2138.9	0.6
	8_{2}	8_{4}	2173.4	0.6
R				
	8_{-3}	9_{-5}	2108.3	0.5
	8_{-7}	9_{-9}	2122.3	3.8
	8_{-8}	9_{-8}	2122.6	7.7
	8_{-5}	9_{-7}	2123.2	1.7
	8_{-6}	9_{-6^q}	2130.2	3.8
	8_{-4}	9_{-4}	2152.7	2.0
	8_{-2}	9_{-2}	2193.3	1.5
	8_{-3}	9_{-1}	2212.1	0.8
	8_{-5}	9_{-3}	2213.0	0.5

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]_J^{J''}$ x 10
	8_0	9_0	82234.8	1.6
	8_{-1}	9_1	2237.4	0.8
	8_2	9_2	2271.4	1.3
	8_1	9_3	2271.6	0.7
	8_4	9_4	2308.9	0.9
	8_3	9_5	2308.9	0.5
	8_6	9_6	2348.7	0.6
P				
	9_0	8_0	1851.0	0.6
	9_{-2}	8_{-2}	1865.4	0.7
	9_{-4}	8_{-4}	1895.1	1.0
	9_{-6}	8_{-6}	1926.5	2.2
	9_{-7}	8_{-5}	1934.7	1.2
	9_{-8}	8_{-8}	1946.2	4.9
	9_{-9}	8_{-7}	1946.6	2.5
Q				
	9_{-6}	9_{-8}	1947.6	1.0
	9_{-7}	9_{-9}	1948.8	0.5
	9_0	9_{-2}	1949.0	0.7
	9_{-4}	9_{-6}	1954.0	1.4
	9_{-2}	9_{-4}	1954.2	1.2
	9_{-5}	9_{-7}	1962.7	0.9
	9_{-1}	9_{-3}	1963.5	0.8
	9_{-3}	9_{-5}	1971.7	1.2
	9_{-5}	9_{-3}	2052.5	0.8

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION		FREQUENCY	*RELATIVE INTENSITY
Branch	$J''_{\tau''}$ $J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	9_{-7} 9_{-5}	82071.8	0.7
	9_{-3} 9_{-1}	2075.5	0.5
	9_{-6} 9_{-4}	2095.8	1.5
	9_{-4} 9_{-2}	2100.8	1.2
	9_{-9} 9_{-7}	2103.8	0.6
	9_{-8} 9_{-6}	2108.0	1.3
	9_{-2} 9_{0}	2125.1	0.8
	9_{0} 9_{2}	2159.5	0.5
R			
	9_{-4} 10_{-6}	2112.9	0.8
	9_{-8} 10_{-10}	2122.4	5.5
	9_{-9} 10_{-9}	2122.5	2.7
	9_{-6} 10_{-8}	2124.4	2.5
	9_{-7} 10_{-7}	2128.2	1.3
	9_{-5} 10_{-5}	2145.0	0.7
	9_{-4} 10_{-2}	2215.0	0.9
	9_{-6} 10_{-4}	2227.5	0.5
	9_{-2} 10_{0}	2235.1	0.9
	9_{0} 10_{2}	2268.6	0.8
	9_{2} 10_{4}	2306.2	0.5
P			
	10_{-7} 9_{-7}	1909.3	0.8
	10_{-6} 9_{-4}	1912.2	0.7
	10_{-8} 9_{-6}	1914.2	1.6
	10_{-9} 9_{-9}	1927.9	1.7

APPX. III

TABLE III.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY
Branch	$J''_{\tau''}$ $J'_{\tau'}$	$\nu(cm^{-1})$	$[I]^{J''}_{J'}$ x 10
	10_{-10} 9_{-8}	81928.1	3.4
Q			
	10_{-8} 10_{-10}	1928.6	0.6
	10_{0} 10_{-2}	1936.8	0.5
	10_{-6} 10_{-8}	1940.7	1.0
	10_{-2} 10_{-4}	1949.7	1.0
	10_{-4} 10_{-6}	1952.7	1.4
	10_{-6} 10_{-4}	2043.8	0.9
	10_{-4} 10_{-2}	2054.7	0.6
	10_{-8} 10_{-6}	2073.1	0.8
	10_{-10} 10_{-8}	2104.9	0.7
R			
	10_{-9} 11_{-11}	2121.6	1.9
	10_{-10} 11_{-10}	2121.6	3.7
	10_{-7} 11_{-9}	2123.9	0.9
	10_{-8} 11_{-8}	2126.0	1.8
	10_{-6} 11_{-6}	2137.6	0.9
	10_{-4} 11_{-4}	2171.4	0.5

APPENDIX IV

TABLE IV.1

Rotation-Electronic Energy Levels of the $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$ States of H_2O. (Electronic Interaction Included)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
0_0	80624.67	82058.67
1_{-1}	0645.86	2079.90
1_0	0659.13	2097.44
1_1	0663.20	2101.72
2_{-2}	0687.44	2121.69
2_{-1}	0697.45	2135.64
2_0	0709.65	2148.47
2_1	0749.52	2201.05
2_2	0750.32	2201.74
3_{-3}	0747.99	2182.75
3_{-2}	0754.45	2192.54
3_{-1}	0778.76	2218.13
3_0	0813.09	2264.76
3_1	0816.91	2268.10
3_2	0890.29	2363.35
3_3	0890.39	2363.42
4_{-4}	0826.11	2261.66
4_{-3}	0829.74	2267.74
4_{-2}	0869.73	2310.02
4_{-1}	0897.22	2349.17

APPX. IV

TABLE IV.1 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
4_0	80907.67	82358.55
4_1	0976.40	2449.49
4_2	0977.09	2449.98
4_3	1082.93	2586.64
4_4	1082.94	2586.64
5_{-5}	0921.07	2357.44
5_{-4}	0922.89	2360.86
5_{-3}	0981.28	2423.12
5_{-2}	1001.39	2453.83
5_{-1}	1022.76	2473.57
5_0	1084.21	2557.41
5_1	1086.84	2559.31
5_2	1190.66	2693.36
5_3	1190.75	2693.41
5_4	1327.91	2867.92
5_5	1327.91	2867.92
6_{-6}	1032.75	2469.77
6_{-5}	1033.60	2471.55
6_{-4}	1111.78	2555.98
6_{-3}	1125.02	2578.21
6_{-2}	1161.49	2612.84

APPX. IV

TABLE IV.1 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
6_{-1}	81213.54	82687.00
6_0	1220.78	2692.38
6_1	1320.41	2823.07
6_2	1320.86	2823.33
6_3	1457.09	2997.09
6_4	1457.10	2997.10
6_5	1625.55	3209.95
6_6	1625.55	3209.95
7_{-7}	1161.28	2598.69
7_{-6}	1161.66	2599.57
7_{-5}	1259.66	2707.01
7_{-4}	1267.48	2721.73
7_{-3}	1322.63	2775.43
7_{-2}	1363.98	2837.99
7_{-1}	1379.83	2850.28
7_0	1472.31	2974.92
7_1	1473.89	2975.87
7_2	1608.30	3148.23
7_3	1608.36	3148.26
7_4	1776.17	3360.57
7_5	1776.17	3360.57
7_6	1976.12	3611.45
7_7	1976.12	3611.45

TABLE IV.1 (Continued)

APPX. IV ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
8_{-8}	81306.79	82744.34
8_{-7}	1306.95	2744.76
8_{-6}	1424.01	2874.89
8_{-5}	1428.23	2883.85
8_{-4}	1504.56	2960.04
8_{-3}	1534.98	3009.95
8_{-2}	1564.11	3033.67
8_{-1}	1646.33	3149.00
8_0	1650.75	3151.70
8_1	1781.74	3321.52
8_2	1782.00	3321.65
8_3	1948.77	3533.10
8_4	1948.78	3533.10
8_5	2148.20	3783.51
8_6	2148.20	3783.51
8_7	2379.94	4072.10
8_8	2379.94	4072.10
9_{-9}	1469.34	2906.82
9_{-8}	1469.40	2907.02
9_{-7}	1604.70	3058.97
9_{-6}	1606.82	3064.05
9_{-5}	1705.40	3165.03
9_{-4}	1725.88	3202.33

APPX. IV

TABLE IV.1 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
9_{-3}	1772.78	3242.41
9_{-2}	1842.27	3345.23
9_{-1}	1852.57	3351.79
9_0	1977.58	3517.16
9_1	1978.47	3517.59
9_2	2143.54	3727.72
9_3	2143.58	3727.74
9_4	2342.21	3977.46
9_5	2342.21	3977.46
9_6	2573.47	4265.62
9_7	2573.47	4265.62
9_8	2837.28	4591.64
9_9	2837.28	4591.64
10_{-10}	1648.97	3086.21
10_{-9}	1648.99	3086.30
10_{-8}	1801.90	3261.94
10_{-7}	1802.92	3348.41
10_{-6}	1923.41	3348.41
10_{-5}	1935.98	3388.61
10_{-4}	2004.34	3475.54
10_{-3}	2059.72	3563.39
10_{-2}	2080.28	3577.22
10_{-1}	2195.93	3735.30

APPX. IV

TABLE IV.1 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
10_0	82198.42	83736.56
10_1	2360.67	3944.60
10_2	2360.82	3944.66
10_3	2558.31	4193.43
10_4	2558.32	4193.43
10_5	2788.90	4480.99
10_6	2788.90	4480.99
10_7	3052.27	4806.61
10_8	3052.27	4806.61
10_9	3259.22	5169.77
10_{10}	3414.49	5169.77
11_{-11}	1845.69	3282.52
11_{-10}	1845.70	3282.56
11_{-9}	2015.86	3475.83
11_{-8}	2016.32	3477.24
11_{-7}	2157.55	3629.14
11_{-6}	2164.64	3645.80
11_{-5}	2256.91	3731.62
11_{-4}	2298.10	3803.09
11_{-3}	2333.97	3828.85
11_{-2}	2436.75	3976.02
11_{-1}	2442.81	3979.21
11_0	2600.37	4183.95

APPX. IV

TABLE IV.1 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
11_1	82600.83	84184.14
11_2	2796.68	4431.57
11_3	2796.70	4431.58
11_4	3026.38	4718.34
11_5	3026.38	4718.34
11_6	3289.14	5043.42
11_7	3289.14	5043.42
11_8	3584.87	5406.20
11_9	3584.87	5406.20
11_{10}	3913.60	5806.26
11_{11}	3913.60	5806.26

APPX.IV TABLE IV.2

Rotation-Electronic Energy Levels of the $\tilde{C}^1B_1$ and $\tilde{D}^1A_1$ States of D_2O. (Electronic Interaction Included)

ENERGY LEVEL J'_τ	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
0_0	80751.9	82074.9
1_{-1}	0762.6	2085.6
1_0	0770.9	2095.3
1_1	0772.8	2097.3
2_{-2}	0783.8	2106.8
2_{-1}	0790.5	2114.8
2_0	0796.2	2120.7
2_1	0821.2	2149.8
2_2	0821.4	2150.1
3_{-3}	0814.8	2138.0
3_{-2}	0819.7	2143.9
3_{-1}	0831.0	2155.7
3_0	0853.3	2182.0
3_1	0854.7	2183.4
3_2	0899.9	2235.7
3_3	0899.9	2235.7
4_{-4}	0855.2	2178.5
4_{-3}	0858.3	2182.4
4_{-2}	0877.0	2202.0
4_{-1}	0896.0	2224.8
4_0	0899.9	2228.5
4_1	0943.3	2279.1

APPX. IV

TABLE IV.2(Continued)

ENERGY LEVEL J_{τ}'	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
4_2	80943.5	82279.2
4_3	1007.9	2353.4
4_4	1007.9	2353.4
5_{-5}	0904.4	2227.8
5_{-4}	0906.2	2230.2
5_{-3}	0933.8	2259.1
5_{-2}	0949.0	2277.9
5_{-1}	0957.3	2286.0
5_0	0997.7	2333.5
5_1	0998.4	2334.1
5_2	1062.1	2407.7
5_3	1062.1	2407.7
5_4	1145.2	2503.3
5_5	1145.2	2503.3
6_{-6}	0962.2	2285.7
6_{-5}	0963.2	2287.1
6_{-4}	1000.8	2326.7
6_{-3}	1012.1	2341.1
6_{-2}	1026.8	2355.6
6_{-1}	1062.9	2398.9
6_0	1065.1	2400.6
6_1	1127.4	2473.0
6_2	1127.5	2473.1

APPX. IV

TABLE IV.2 (Continue)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
6_3	1210.2	2568.4
6_4	1210.2	2568.4
6_5	1311.8	2685.1
6_6	1311.8	2685.1
7_{-7}	1028.7	2352.2
7_{-6}	1029.2	2353.0
7_{-5}	1077.3	2403.9
7_{-4}	1085.0	2414.2
7_{-3}	1108.1	2437.1
7_{-2}	1139.0	2475.0
7_{-1}	1143.9	2479.3
7_0	1203.8	2549.5
7_1	1204.2	2549.7
7_2	1286.3	2644.5
7_3	1286,3	2644.5
7_4	1387.7	2761.0
7_5	1387.7	2761.0
7_6	1507.9	2898.9
7_7	1507.9	2898.9
8_{-8}	1104.0	2427.4
8_{-7}	1104.2	2427.7
8_{-6}	1162.6	2490.1
8_{-5}	1167.5	2496.9

APPX. IV

TABLE IV.2 (Continued)

ENERGY LEVEL $J'_{\tau'}$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
8_{-4}	81200.5	82530.1
8_{-3}	1225.8	2561.9
8_{-2}	1235.4	2570.5
8_{-1}	1291.4	2637.0
8_0	1292.4	2637.8
8_1	1373.5	2731.7
8_2	1373.6	2731.7
8_3	1474.6	2847.9
8_4	1474.6	2847.9
8_5	1594.6	2985.7
8_6	1594.6	2985.7
8_7	1733.5	3144.7
8_8	1733.5	3144.7
9_{-9}	1187.9	2511.2
9_{-8}	1188.1	2511.3
9_{-7}	1256.6	2584.9
9_{-6}	1259.4	2589.1
9_{-5}	1303.5	2634.0
9_{-4}	1323.0	2659.4
9_{-3}	1339.4	2674.5
9_{-2}	1390.1	2735.8
9_{-1}	1392.5	2737.7

APPX.IV

TABLE IV.2 (Continued)

ENERGY LEVEL J'_{τ}	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
9_0	81471.9	82830.1
9_1	1472.1	2830.2
9_2	1572.6	2945.9
9_3	1572.6	2945.9
9_4	1692.3	3083.4
9_5	1692.3	3083.8
9_6	1831.0	3242,2
9_7	1831.0	3242.2
9_8	1988.6	3422.3
9_9	1988.6	3422.3
10_{-10}	1280.7	2603.7
10_{-9}	1280.8	2603.8
10_{-8}	1358.9	2688.0
10_{-7}	1360.5	2690.5
10_{-6}	1460.3	2748.1
10_{-5}	1430.3	2767.1
10_{-4}	1455.7	2791.0
10_{-3}	1499.8	2845.7
10_{-2}	1505.1	2849.9
10_{-1}	1581.6	2939.7
10_0	1582.0	2940.0
10_1	1681.7	3055.0
10_2	1681.7	3055.0

APPX.IV

TABLE IV.2 (Continued)

ENERGY LEVEL J'_τ	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
10_3	81801.1	83192.1
10_4	1801.1	3192.1
10_5	1939.6	3350.7
10_6	1939.6	3350.7
10_7	2097.0	3530.7
10_8	2097.0	3530.7
10_9	2273.3	3731.7
10_{10}	2273.3	3731.7
11_{-11}	1382.3	2704.9
11_{-10}	1382.3	2705.0
11_{-9}	1469.8	2799.6
11_{-8}	1470.7	2801.0
11_{-7}	1538.2	2871.3
11_{-6}	1547.5	2884.8
11_{-5}	1583.7	2919.5
11_{-4}	1620.5	2966.6
11_{-3}	1630.4	2974.8
11_{-2}	1702.5	3060.7
11_{-1}	1703.6	3061.5
11_0	1802.0	3175.4
11_1	1802.1	3175.4
11_2	1920.9	3312.0
11_3	1920.9	3312.0

APPX.IV

TABLE IV.2 (Continued)

ENERGY LEVEL $J_{\sim}'$	EXCITED STATE $\tilde{C}^1B_1$ E' (cm^{-1})	EXCITED STATE $\tilde{D}^1A_1$ E' (cm^{-1})
11_4	82059.1	83470.3
11_5	2059.1	3470.3
11_6	2216.3	3650.0
11_7	2216.3	3650.0
11_8	2392.5	3850.9
11_9	2392.5	3850.9
11_{10}	2587.7	4072.9
11_{11}	2587.7	4072.9

APPENDIX V

TABLE V.1

$\tilde{C}^1B_1$ Transitions in H_2O Calculated for Various Ratios $\langle\mu_z\rangle : \langle\mu_x\rangle$. (Electronic Interactions)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
R	0_0	1_1	80663.2	-	3.3	3.5	3.1
P	1_1	0_0	582.3	-	8.1	8.1	8.1
Q							
	1_0	1_{-1}	608.7	-	4.2	4.2	4.2
	1_{-1}	1_0	635.3	-	13.3	14.4	12.3
R							
	1_1	2_{-2}	645.0	-	2.6	2.5	2.7
	1_{-1}	2_0	685.9	-	13.3	14.4	12.3
	1_1	2_2	707.9	-	13.6	15.6	11.7
	1_0	2_1	712.4	-	4.1	4.8	3.5
P							
	2_1	1_0	523.8	-	7.7	7.1	8.3
	2_2	1_1	526.6	-	2.9	2.7	3.1
	2_0	1_{-1}	550.6	-	3.1	3.1	3.1
	2_{-2}	1_1	593.1	-	0.7	0.8	0.6
Q							
	2_2	2_{-2}	560.9	-	0.8	0.7	0.9
	2_1	2_0	574.3	-	4.3	3.9	4.6
	2_{-1}	2_{-2}	607.9	-	19.0	19.1	18.8
	2_{-2}	2_{-2}	627.3	-	6.7	7.2	6.3
	2_0	2_1	654.3	-	1.7	2.0	1.5
	2_{-1}	2_2	670.8	-	3.6	4.3	2.9
R							
	2_1	3_{-2}	619.1	-	0.5	-	0.6

*Values of $[I]_{J'}^{J''}$ x 10 less than 0.5 are not included for $\langle\mu_z\rangle : \langle\mu_x\rangle$ = 0:1 and the corresponding cases of 1:0, 1:1 and 1:-1 in this table.

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	2_0	3_{-3}	80652.8	-	0.9	0.9	1.0
	2_{-2}	3_{-1}	708.6	-	4.3	4.7	4.0
	2_0	3_1	721.7	-	4.6	5.2	4.0
	2_{-1}	3_0	733.6	-	11.2	13.0	9.5
	2_2	3_3	753.8	-	4.3	5.4	3.4
	2_1	3_2	755.0	-	13.0	16.2	10.2
P							
	3_2	2_1	462.2	-	2.1	1.8	2.4
	3_3	2_2	462.8	-	6.3	5.4	7.3
	3_0	2_{-2}	490.7	-	2.0	1.9	2.2
	3_1	2_0	497.1	-	8.1	7.7	8.5
	3_{-1}	2_{-2}	513.9	-	8.0	7.9	8.1
	3_{-3}	2_0	572.7	-	1.8	2.2	1.5
	3_{-1}	2_2	576.8	-	0.8	0.9	0.6
Q							
	3_3	3_0	525.6	-	1.6	1.3	2.0
	3_2	3_1	529.6	-	0.6	0.5	0.7
	3_1	3_{-2}	541.9	-	1.7	1.4	2.0
	3_0	3_{-1}	572.1	-	1.9	1.8	2.1
	3_{-2}	3_{-3}	605.6	-	7.4	7.5	7.3
	3_{-3}	3_{-2}	617.5	-	23.4	24.7	22.2
	3_{-1}	3_0	639.6	-	7.0	8.0	6.1
	3_{-2}	3_1	674.5	-	1.0	1.3	0.8

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	3_1	3_2	80677.7	-	2.6	3.2	2.0
	3_0	3_3	683.7	-	0.9	1.1	0.6
R							
	3_1	4_{-4}	652.6	-	1.9	1.7	2.1
	3_1	4_{-2}	657.2	-	2.1	2.0	2.3
	3_{-3}	4_{-2}	732.8	-	10.0	11.1	8.9
	3_{-1}	4_0	734.1	-	12.1	13.6	10.7
	3_{-2}	4_{-1}	754.9	-	3.0	3.5	2.5
	3_1	4_2	764.5	-	10.0	12.2	8.0
	3_0	4_1	769.7	-	3.4	4.1	2.7
	3_3	4_4	795.4	-	8.5	11.2	6.1
	3_2	4_3	795.6	-	2.8	3.8	2.0
P							
	4_3	3_2	395.7	-	3.1	2.5	3.9
	4_4	3_3	396.8	-	1.0	0.8	1.3
	4_1	3_0	428.6	-	4.3	3.7	4.9
	4_2	3_1	431.1	-	1.5	1.3	1.7
	4_{-1}	3_{-2}	453.6	-	4.2	3.8	4.5
	4_0	3_{-1}	462.3	-	2.1	2.0	2.2
	4_{-2}	4_{-3}	472.0	-	1.8	1.7	1.8
	4_{-3}	3_0	588.0	-	0.5	0.7	0.4
Q							
	4_3	4_2	482.5	-	0.6	0.5	0.8
	4_2	4_{-1}	511.4	-	0.5	-	0.6
	4_1	4_0	523.1	-	2.0	1.6	2.3

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	4_{-1}	4_{-2}	80568.8	-	5.9	5.6	6.1
	4_{-3}	4_{-4}	601.0	-	21.1	21.7	20.6
	4_{-4}	4_{-3}	607.4	-	7.3	7.6	7.0
	4_{-2}	4_{-1}	621.2	-	2.3	2.6	2.1
	4_{0}	4_{1}	659.9	-	0.9	1.1	0.7
	4_{-1}	4_{2}	676.2	-	2.7	3.4	2.0
	4_{-3}	4_{0}	682.6	-	1.7	2.2	1.3
	4_{1}	4_{4}	698.4	-	1.1	1.5	0.8
R							
	4_{-1}	5_{-4}	622.0	-	0.5	-	0.7
	4_{0}	5_{-3}	664.8	-	0.7	0.6	0.7
	4_{-2}	5_{-1}	746.7	-	2.9	3.3	2.5
	4_{-4}	5_{-3}	758.9	-	2.2	2.5	1.9
	4_{0}	5_{1}	770.4	-	2.3	2.8	1.9
	4_{-3}	5_{-2}	776.3	-	6.3	7.5	5.2
	4_{-1}	5_{0}	783.3	-	7.0	8.6	5.5
	4_{2}	5_{3}	804.9	-	1.9	2.4	1.4
	4_{1}	5_{2}	806.1	-	5.6	7.4	4.1
	4_{4}	5_{5}	833.3	-	1.3	1.8	0.9
	4_{3}	5_{4}	833.3	-	3.9	5.5	2.6
P							
	5_{5}	4_{4}	325.3	-	1.1	0.8	1.4
	5_{2}	4_{1}	360.0	-	0.6	0.5	0.8
	5_{3}	4_{2}	360.5	-	1.9	1.5	2.3

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	5_0	4_{-1}	80391.0	-	0.9	0.8	1.0
	5_1	4_0	396.6	-	2.9	2.6	3.2
	5_{-2}	4_{-3}	412.6	-	0.8	0.8	0.9
	5_{-1}	4_{-2}	421.8	-	4.0	3.8	4.1
	5_{-3}	4_{-4}	425.5	-	3.0	2.8	3.1
	5_{-3}	4_0	507.1	-	0.8	1.0	0.6
	5_{-5}	4_{-2}	543.8	-	0.5	0.7	-
Q							
	5_3	5_0	467.6	-	0.6	-	0.8
	5_1	5_{-2}	490.3	-	0.8	0.6	1.1
	5_0	5_{-1}	516.6	-	0.5	-	0.6
	5_{-2}	5_{-3}	564.2	-	1.6	1.6	1.7
	5_{-4}	5_{-5}	594.0	-	5.6	5.8	5.5
	5_{-5}	5_{-4}	597.0	-	17.2	17.9	16.5
	5_{-3}	5_{-2}	600.8	-	5.7	6.2	5.3
	5_{-1}	5_0	636.3	-	2.1	2.6	1.7
	5_{-2}	5_1	669.7	-	0.6	0.8	0.4
	5_1	5_2	679.6	-	1.1	1.5	0.8
R							
	5_1	6_{-2}	650.4	-	0.7	0.6	0.8
	5_{-1}	6_{-4}	663.9	-	1.2	1.1	1.4
	5_{-3}	6_{-2}	760.9	-	5.1	5.8	4.4
	5_{-1}	6_0	772.9	-	4.3	5.1	3.6
	5_{-5}	6_{-4}	785.9	-	3.9	4.6	3.3

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	5_{-2}	6_{-1}	80796.4	-	1.4	1.7	1.1
	5_{-4}	6_{-3}	797.9	-	1.3	1.6	1.1
	5_{1}	6_{2}	809.8	-	3.2	4.2	2.4
	5_{0}	6_{1}	814.2	-	1.1	1.5	0.9
	5_{3}	6_{4}	840.5	-	2.2	3.1	1.5
	5_{2}	6_{3}	840.7	-	0.7	1.0	0.5
	5_{5}	6_{6}	867.9	-	1.3	1.9	0.8
P							
	6_{3}	5_{2}	287.0	-	0.6	-	0.7
	6_{1}	5_{0}	321.0	-	1.0	0.8	1.2
	6_{-1}	5_{-2}	349.5	-	1.4	1.2	1.6
	6_{0}	5_{-1}	357.9	-	0.6	0.5	0.6
	6_{-3}	5_{-4}	368.5	-	1.3	1.2	1.5
	6_{-2}	5_{-3}	375.8	-	0.7	0.7	0.7
Q							
	6_{-1}	6_{-2}	509.6	-	1.0	0.9	1.2
	6_{-3}	6_{-4}	557.3	-	3.6	3.5	3.6
	6_{-4}	6_{-3}	580.2	-	1.3	1.4	1.3
	6_{-5}	6_{-6}	584.7	-	11.6	11.9	11.2
	6_{-6}	6_{-5}	586.0	-	3.9	4.0	3.8
	6_{-3}	6_{0}	666.3	-	0.9	1.1	0.6
	6_{-1}	6_{2}	669.0	-	0.7	1.0	0.5
R							
	6_{-2}	7_{-1}	774.3	-	0.8	0.9	0.6
	6_{-4}	7_{-3}	777.8	-	0.8	1.0	0.7

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	6_0	7_1	80809.1	-	0.6	0.7	-
	6_{-3}	7_{-2}	809.5	-	2.3	2.9	1.8
	6_{-6}	7_{-5}	812.1	-	0.7	0.9	0.6
	6_{-5}	7_{-4}	819.4	-	2.2	2.8	1.7
	6_{-1}	7_0	820.4	-	1.8	2.3	1.3
	6_1	7_2	845.1	-	1.2	1.6	0.8
	6_3	7_4	872.5	-	0.7	1.0	-
P							
	7_{-1}	6_{-2}	313.8	-	0.8	0.7	0.9
	7_{-3}	6_{-4}	324.7	-	0.9	0.8	0.9
	7_{-5}	6_{-6}	325.6	-	0.7	0.6	0.7
Q							
	7_{-4}	7_{-5}	547.6	-	0.7	0.7	0.7
	7_{-5}	7_{-4}	560.3	-	2.4	2.5	2.3
	7_{-6}	7_{-7}	573.4	-	2.3	2.4	2.2
	7_{-7}	7_{-6}	574.0	-	7.0	7.2	6.7
	7_{-3}	7_{-2}	576.9	-	0.8	0.9	0.7
R							
	7_{-3}	8_{-2}	777.0	-	1.1	1.2	0.9
	7_{-5}	8_{-4}	797.4	-	1.1	1.3	0.9
	7_{-1}	8_0	803.1	-	0.7	0.9	0.6
	7_{-7}	8_{-6}	836.4	-	1.1	1.4	0.9
	7_1	8_2	843.3	-	0.5	0.7	-
Q							
	8_{-5}	8_{-6}	534.7	-	1.2	1.2	1.2

APPX V

TABLE V.1 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	8_{-7}	8_{-8}	80560.6	-	3.7	3.8	3.6
	8_{-8}	8_{-7}	560.8	-	1.2	1.3	1.2
R	8_{-7}	9_{-6}	860.6	-	0.5	0.7	-
Q							
	9_{-7}	9_{-6}	522.1	-	0.6	0.6	0.6
	9_{-8}	9_{-9}	546.1	-	0.6	0.6	0.6
	9_{-9}	9_{-8}	546.2	-	1.8	1.8	1.7
Q	10_{-9}	10_{-10}	530.2	-	0.8	0.8	0.7

APPX V TABLE V.2

$\tilde{D}^1A_1$ Transitions in H_2O Calculated for Various Ratios $\langle\mu_z\rangle : \langle\mu_x\rangle$. (Electronic Interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
R	0_0	1_0	82097.4	3.3	-	3.1	3.6
P	1_0	0_0	2021.5	2.8	-	2.8	2.8
Q							
	1_1	1_{-1}	2037.5	12.2	-	12.2	12.2
	1_{-1}	1_1	2077.9	13.3	-	12.3	14.4
R							
	1_0	2_{-2}	2084.5	1.9	-	1.8	1.9
	1_{-1}	2_{-1}	2111.8	13.3	-	12.3	14.4
	1_1	2_1	2158.7	12.1	-	10.3	14.1
	1_0	2_2	2164.6	3.7	-	3.1	4.3
P							
	2_2	1_0	1960.9	2.1	-	2.3	1.9
	2_1	1_1	1966.4	7.7	-	8.3	7.1
	2_{-1}	1_{-1}	2000.4	10.2	-	10.2	10.2
	2_{-2}	1_0	2027.3	1.8	-	1.7	1.9
Q							
	2_1	2_{-1}	2000.3	4.3	-	4.6	3.9
	2_2	2_0	2011.9	2.1	-	2.2	2.0
	2_0	2_{-2}	2026.5	4.6	-	4.7	4.6
	2_{-2}	2_0	2078.3	4.9	-	4.5	5.3
	2_0	2_2	2106.5	2.3	-	2.0	2.6
	2_{-1}	2_1	2121.5	5.6	-	4.8	6.5

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included for $\langle\mu_z\rangle : \langle\mu_x\rangle$ = 1:0 and the corresponding cases of 0:1, 1:1 and 1:-1 in this table.

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
R							
	2_1	3_{-1}	82082.8	1.3	-	1.3	1.2
	2_{-1}	3_{-3}	2103.2	10.3	-	10.0	10.7
	2_{-2}	3_{-2}	2122.4	5.1	-	4.7	5.5
	2_0	3_0	2169.5	3.5	-	2.9	4.0
	2_{-1}	3_1	2188.6	7.7	-	6.3	9.1
	2_2	3_2	2226.8	4.1	-	3.2	5.1
	2_1	3_3	2228.1	12.3	-	9.5	15.4
P							
	3_3	2_1	1913.6	5.7	-	6.7	4.8
	3_2	2_2	1914.4	1.9	-	2.3	1.6
	3_1	2_{-1}	1923.1	3.2	-	3.7	2.9
	3_0	2_0	1941.8	2.0	-	2.2	1.9
	3_{-2}	2_{-2}	1979.3	3.5	-	3.5	3.5
	3_{-3}	2_{-1}	1998.7	8.9	-	8.6	9.2
	3_{-1}	2_1	2027.5	1.3	-	1.2	1.4
Q							
	3_2	3_0	1977.5	0.8	-	0.9	0.7
	3_3	3_1	1980.6	2.7	-	3.0	2.4
	3_0	3_{-2}	1985.8	1.6	-	1.8	1.5
	3_1	3_{-1}	2005.6	9.3	-	9.7	9.0
	3_{-1}	3_{-3}	2009.2	11.0	-	11.3	10.7
	3_{-3}	3_{-1}	2081.2	11.1	-	9.8	12.3
	3_{-1}	3_1	2094.6	9.1	-	7.9	10.4
	3_{-2}	3_0	2122.4	2.1	-	1.8	2.5
	3_1	3_3	2150.8	3.4	-	2.8	4.2

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	3_0	3_2	82156.7	1.2	-	0.9	1.4
R							
	3_0	4_{-2}	2103.3	0.8	-	0.8	0.8
	3_{-2}	4_{-4}	2119.3	4.2	-	4.0	4.4
	3_{-3}	4_{-3}	2130.8	15.1	-	14.1	16.2
	3_{-1}	4_{-1}	2175.6	8.3	-	7.1	9.6
	3_{-2}	4_0	2216.2	1.5	-	1.2	1.8
	3_1	4_1	2236.9	8.2	-	6.3	10.3
	3_0	4_2	2243.3	2.8	-	2.2	3.5
	3_3	4_3	2298.1	8.2	-	5.8	10.9
	3_2	4_4	2298.3	2.7	-	1.9	3.6
P							
	4_4	3_2	1868.7	1.0	-	1.2	0.8
	4_3	3_3	1868.8	3.0	-	3.7	2.3
	4_2	3_0	1878.9	1.1	-	1.3	0.9
	4_1	3_1	1883.6	3.6	-	4.2	0.3
	4_{-1}	3_{-1}	1917.2	4.4	-	4.7	4.1
	4_{-3}	3_{-3}	1957.7	9.5	-	9.5	9.6
	4_{-4}	3_{-2}	1970.2	3.2	-	3.1	3.2
	4_{-2}	3_0	1988.7	0.7	-	0.7	0.7
	4_{-3}	3_1	2043.0	0.8	-	0.7	0.9
Q							
	4_3	4_1	1954.9	0.9	-	1.1	0.8
	4_1	4_{-1}	1964.6	2.9	-	3.3	2.5
	4_{-1}	4_{-3}	1966.8	3.9	-	4.3	3.4

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	4_2	4_0	81972.7	1.1	-	1.3	1.0
	4_{-2}	4_{-4}	1985.6	2.3	-	2.4	2.1
	4_0	4_{-2}	1993.6	2.8	-	2.9	2.8
	4_{-2}	4_0	2082.5	2.6	-	2.3	3.0
	4_{-4}	4_{-2}	2087.7	2.2	-	1.9	2.5
	4_{-3}	4_{-1}	2124.1	5.1	-	4.2	6.2
	4_0	4_2	2133.5	1.2	-	1.0	1.5
	4_{-1}	4_1	2148.6	3.9	-	3.1	4.8
	4_2	4_4	2199.8	0.5	-	0.4	0.6
	4_1	4_3	2201.1	1.5	-	1.1	1.9
R							
	4_1	5_{-1}	2089.0	0.5	-	0.5	0.5
	4_{-1}	5_{-3}	2122.2	2.8	-	2.7	2.9
	4_{-3}	5_{-5}	2132.4	12.0	-	11.4	12.6
	4_{-4}	5_{-4}	2138.5	4.4	-	4.1	4.6
	4_{-2}	5_{-2}	2177.8	2.1	-	1.8	2.4
	4_0	5_0	2240.9	1.6	-	1.3	2.1
	4_{-3}	5_{-1}	2248.5	2.2	-	1.7	2.7
	4_{-1}	5_1	2258.4	5.1	-	3.8	6.5
	4_2	5_2	2307.5	1.6	-	1.2	2.2
	4_1	5_3	2308.9	5.0	-	3.5	6.7
	4_4	5_4	2373.3	1.3	-	0.8	1.8
	4_3	5_5	2373.3	3.8	-	2.5	5.3
P							
	5_5	4_3	1828.0	1.0	-	1.4	0.7

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	5_3	4_1	81832.9	1.6	-	2.0	1.2
	5_2	4_2	1833.6	0.5	-	0.7	-
	5_1	4_{-1}	1838.1	1.5	-	1.8	1.2
	5_0	4_0	1852.4	0.7	-	0.8	0.5
	5_{-2}	4_{-2}	1892.9	1.0	-	1.1	0.9
	5_{-4}	4_{-4}	1934.6	2.5	-	2.5	2.6
	5_{-5}	4_{-3}	1941.8	7.8	-	7.7	8.0
	5_{-3}	4_{-1}	1948.6	2.3	-	2.2	2.3
	5_{-1}	4_0	2001.6	0.5	-	0.5	0.6
Q							
	5_3	5_1	1942.7	1.0	-	1.2	0.9
	5_{-2}	5_{-4}	1943.8	0.8	-	0.9	0.7
	5_0	5_{-2}	1947.6	0.7	-	0.8	0.6
	5_{-3}	5_{-5}	1956.9	3.5	-	3.8	3.2
	5_1	5_{-1}	1962.5	3.1	-	3.3	2.8
	5_{-1}	5_{-3}	1975.2	5.7	-	5.9	5.5
	5_{-3}	5_{-1}	2073.0	5.0	-	4.3	5.8
	5_{-5}	5_{-3}	2097.2	3.6	-	3.0	4.3
	5_{-1}	5_1	2111.4	2.8	-	2.3	3.4
	5_{-4}	5_{-2}	2126.7	1.1	-	0.9	1.4
	5_{-2}	5_0	2140.3	1.0	-	0.8	1.2
	5_1	5_3	2182.3	1.4	-	1.1	1.8
	5_0	5_2	2187.2	0.5	-	-	0.6
	5_3	5_5	2251.3	0.5	-	-	0.7

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
R							
	5_{-2}	6_{-4}	82138.9	0.9	-	0.8	0.9
	5_{-4}	6_{-6}	2142.7	3.1	-	3.0	3.3
	5_{-5}	6_{-5}	2145.6	9.8	-	9.2	10.4
	5_{-3}	6_{-3}	2177.6	4.2	-	3.7	4.8
	5_{-1}	6_{-1}	2239.1	2.7	-	2.1	3.4
	5_{-2}	6_{0}	2275.3	0.9	-	0.6	1.1
	5_{1}	6_{1}	2312.0	2.6	-	1.8	3.5
	5_{0}	6_{2}	2317.1	0.9	-	0.6	1.2
	5_{-5}	6_{-1}	2361.1	0.5	-	-	0.6
	5_{3}	6_{3}	2380.5	2.0	-	1.3	2.9
	5_{2}	6_{4}	2380.7	0.7	-	-	1.0
	5_{5}	6_{5}	2452.3	1.3	-	0.8	1.9
P							
	6_{3}	5_{3}	1789.8	0.5	-	0.7	-
	6_{1}	5_{1}	1796.1	0.7	-	0.9	0.6
	6_{-1}	5_{-1}	1821.7	1.0	-	1.2	0.8
	6_{-3}	5_{-3}	1868.7	1.9	-	2.0	1.8
	6_{-4}	5_{-2}	1909.0	0.6	-	0.6	0.6
	6_{-5}	5_{-5}	1909.4	5.3	-	5.3	5.4
	6_{-6}	5_{-4}	1913.3	1.8	-	1.8	1.9
Q							
	6_{-3}	6_{-5}	1917.1	1.4	-	1.6	1.1
	6_{1}	6_{-1}	1923.8	0.7	-	0.9	0.6
	6_{-4}	6_{-6}	1924.9	0.6	-	0.6	0.5

APPX V

TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	6_{-1}	6_{-3}	1926.3	1.4	-	1.6	1.2
	6_{0}	6_{-2}	1948.0	0.7	-	0.8	0.7
	6_{-2}	6_{-4}	1950.5	1.0	-	1.0	0.9
	6_{-4}	6_{-2}	2068.0	0.8	-	0.7	1.0
	6_{-2}	6_{0}	2086.9	0.6	-	0.5	0.7
	6_{-6}	6_{-4}	2108.4	0.6	-	0.5	0.8
	6_{-5}	6_{-3}	2130.1	1.9	-	1.5	2.4
	6_{-3}	6_{-1}	2132.6	1.7	-	1.3	2.2
	6_{-1}	6_{1}	2171.2	1.0	-	0.7	1.3
R							
	6_{-5}	7_{-7}	2150.6	6.4	-	6.0	6.7
	6_{-6}	7_{-6}	2152.0	2.2	-	2.0	2.3
	6_{-3}	7_{-5}	2152.6	2.0	-	1.8	2.1
	6_{-4}	7_{-4}	2176.9	0.9	-	0.8	1.0
	6_{-2}	7_{-2}	2232.5	0.5	-	-	0.6
	6_{-3}	7_{-1}	2295.8	1.1	-	0.8	1.5
	6_{-1}	7_{1}	2324.0	1.3	-	0.9	1.8
	6_{1}	7_{3}	2385.1	1.0	-	0.6	1.4
	6_{3}	7_{5}	2456.9	0.6	-	-	0.9
P							
	7_{-5}	6_{-3}	1871.1	1.2	-	1.1	1.2
	7_{-6}	6_{-6}	1881.9	1.0	-	1.1	1.1
	7_{-7}	6_{-5}	1883.9	3.3	-	3.2	3.4
Q							
	7_{-5}	7_{-7}	1891.5	0.7	-	0.9	0.6

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TABLE V.2 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	7_1	7_{-1}	81911.6	0.5	-	0.6	-
	7_{-3}	7_{-5}	1919.9	1.2	-	1.3	1.1
	7_{-1}	7_{-3}	1927.8	1.1	-	1.2	1.1
	7_{-3}	7_{-1}	2063.2	0.8	-	0.7	1.0
	7_{-5}	7_{-3}	2068.3	1.0	-	0.8	1.2
	7_{-7}	7_{-5}	2119.4	0.9	-	0.7	1.2
R							
	7_{-6}	8_{-8}	2156.5	1.3	-	1.2	1.3
	7_{-7}	8_{-7}	2157.1	3.8	-	3.6	4.0
	7_{-5}	8_{-5}	2176.7	1.5	-	1.3	1.6
	7_{-3}	8_{-3}	2222.8	0.7	-	0.5	0.8
	7_{-1}	8_{-1}	2301.3	0.5	-	-	0.6
P							
	8_{-5}	7_{-5}	1817.7	0.6	-	0.6	0.5
	8_{-7}	7_{-7}	1852.5	1.8	-	1.7	1.8
	8_{-8}	7_{-6}	1853.4	0.6	-	0.6	0.6
Q	8_{-7}	8_{-5}	2137.6	0.5	-	-	0.6
R							
	8_{-7}	9_{-9}	2160.6	2.0	-	1.9	2.1
	8_{-8}	9_{-8}	2160.9	0.7	-	0.6	0.7
	8_{-5}	9_{-7}	2169.7	0.7	-	0.6	0.7
P	9_{-9}	8_{-7}	1821.6	0.8	-	0.8	0.9
R	9_{-9}	10_{-9}	2163.1	0.9	-	0.9	1.0

APPX. V TABLE V.3

$\tilde{C}^1B_1$ Transitions in D_2O Calculated for Various Ratios $\langle\mu_z\rangle : \langle\mu_x\rangle$ (Electronic interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
R	0_0	1_1	80772.8	-	6.7	7.0	6.4
P	1_1	0_0	729.2	-	3.0	3.0	3.0
Q							
	1_0	1_{-1}	742.4	-	9.1	9.1	9.1
	1_{-1}	1_0	758.8	-	4.7	4.9	4.5
R							
	1_1	2_{-2}	761.1	-	1.1	1.0	1.1
	1_{-1}	2_0	784.0	-	4.7	4.9	4.5
	1_1	2_2	798.8	-	4.9	5.3	4.5
	1_0	2_1	800.9	-	9.0	9.9	8.2
P							
	2_1	1_0	697.3	-	3.5	3.3	3.6
	2_2	1_1	698.7	-	7.8	7.5	8.1
	2_0	1_{-1}	713.3	-	7.8	7.8	7.8
	2_{-2}	1_1	736.9	-	1.8	1.9	1.7
Q							
	2_2	2_{-1}	716.4	-	2.5	2.3	2.7
	2_1	2_0	722.5	-	1.9	1.8	2.0
	2_{-1}	2_{-2}	741.7	-	7.4	7.5	7.4
	2_{-2}	2_{-1}	754.6	-	15.6	16.3	15.0
	2_0	2_1	771.8	-	4.4	4.8	4.0

*Values of $[I]^{J''}_{J'}$ x 10 less than 0.5 are not included for $\langle\mu_z\rangle : \langle\mu_x\rangle$ = 0:1 and the corresponding cases of 1:0, 1:1 and 1:-1 in the table.

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TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	2_{-1}	2_2	80779.4	-	1.6	1.8	1.4
R							
	2_2	3_{-1}	756.9	-	1.1	1.0	1.1
	2_0	3_{-3}	765.5	-	2.9	2.8	3.0
	2_{-2}	3_{-1}	795.1	-	10.5	11.0	9.9
	2_0	3_1	805.4	-	11.1	12.0	10.2
	2_{-1}	3_0	811.3	-	4.5	4.9	4.1
	2_2	3_3	825.8	-	11.8	13.4	10.2
	2_1	3_2	826.3	-	5.9	6.7	5.1
P							
	3_2	2_1	664.3	-	7.9	7.2	8.6
	3_3	2_2	664.5	-	4.0	3.6	4.3
	3_0	2_{-1}	680.5	-	6.5	6.2	6.8
	3_1	2_0	683.9	-	4.2	4.1	4.4
	3_{-1}	2_{-2}	694.8	-	4.1	4.1	4.1
	3_{-3}	2_0	725.7	-	1.1	1.2	1.0
	3_{-2}	2_1	746.6	-	0.5	0.5	-
Q							
	3_3	3_0	696.4	-	1.1	1.0	1.2
	3_2	3_1	697.9	-	2.3	2.1	2.6
	3_1	3_{-2}	707.4	-	1.2	1.1	1.3
	3_0	3_{-1}	721.0	-	6.1	5.9	6.4

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION Branch	J''_τ	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$ 1:0	0:1	1:1	1:-1
	3_{-2}	3_{-3}	740.3	-	19.8	20.0	19.6
	3_{-3}	3_{-2}	749.2	-	10.5	10.8	10.1
	3_{-1}	3_{0}	764.4	-	3.5	3.8	3.2
	3_{-2}	3_{1}	780.2	-	3.6	4.1	3.2
	3_{1}	3_{2}	787.7	-	1.5	1.7	1.3
	3_{0}	3_{3}	789.9	-	2.9	3.4	2.5
R							
	3_{0}	4_{-3}	748.3	-	0.8	0.8	0.9
	3_{1}	4_{-2}	764.8	-	1.2	1.1	1.2
	3_{-1}	4_{-4}	766.2	-	1.3	1.2	1.3
	3_{-3}	4_{-2}	806.5	-	4.8	5.1	4.5
	3_{-1}	4_{0}	811.0	-	5.8	6.3	5.4
	3_{-2}	4_{-1}	821.5	-	8.4	9.2	7.6
	3_{1}	4_{2}	831.3	-	5.4	6.1	4.7
	3_{0}	4_{1}	833.3	-	10.8	12.2	9.4
	3_{2}	4_{3}	851.0	-	10.9	12.9	9.0
	3_{3}	4_{4}	850.9	-	5.4	6.5	4.5
P							
	4_{3}	3_{2}	629.2	-	3.1	2.7	3.6
	4_{4}	3_{3}	629.2	-	6.3	5.5	7.2
	4_{1}	3_{0}	647.2	-	3.4	3.1	3.7
	4_{2}	3_{1}	648.2	-	7.0	6.5	7.6

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle\mu_z\rangle:\langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	4_{-1}	3_{-2}	80661.5	-	2.8	2.7	2.9
	4_0	3_{-1}	666.8	-	8.6	8.3	8.8
	4_{-2}	3_{-3}	673.6	-	7.2	7.1	7.2
	4_{-2}	3_1	713.5	-	1.4	1.6	1.2
	4_{-4}	3_{-1}	715.9	-	1.7	1.9	1.5
Q							
	4_4	4_1	672.6	-	1.4	1.1	1.6
	4_3	4_2	672.8	-	0.7	0.6	0.8
	4_2	4_{-1}	689.5	-	2.8	2.4	3.1
	4_1	4_0	693.8	-	1.6	1.4	1.8
	4_0	4_{-3}	694.1	-	1.4	1.2	1.6
	4_{-1}	4_{-2}	718.9	-	3.7	3.6	3.8
	4_{-3}	4_{-4}	737.8	-	11.5	11.6	11.3
	4_{-4}	4_{-3}	743.2	-	24.0	24.7	23.3
	4_{-2}	4_{-1}	754.8	-	8.5	9.1	7.9
	4_0	4_1	779.1	-	4.0	4.6	3.5
	4_{-3}	4_0	782.6	-	1.4	1.6	1.2
	4_{-1}	4_2	785.4	-	2.0	2.3	1.7
	4_2	4_3	801.3	-	1.9	2.3	1.5
	4_1	4_4	801.7	-	1.0	1.2	0.8
R							
	4_{-1}	5_{-4}	748.1	-	0.5	-	0.5

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TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	J''_τ	J'_τ	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	4_2	5_{-1}	80750.8	-	0.9	0.8	1.0
	4_{-2}	5_{-5}	763.2	-	1.8	1.7	2.0
	4_0	5_{-3}	769.6	-	3.0	2.9	3.2
	4_{-2}	5_{-1}	816.2	-	11.0	11.8	10.2
	4_{-4}	5_{-3}	818.7	-	7.8	8.4	7.2
	4_{-3}	5_{-2}	831.6	-	3.6	4.0	3.3
	4_0	5_1	834.2	-	9.4	10.5	8.3
	4_{-1}	5_0	839.5	-	4.7	5.3	4.1
	4_2	5_3	855.6	-	9.0	10.7	7.5
	4_1	5_2	856.0	-	4.5	5.4	3.8
	4_4	5_5	874.5	-	7.9	9.8	6.2
	4_3	5_4	874.5	-	4.0	4.9	3.1
P							
	5_4	4_3	592.6	-	3.9	3.3	4.7
	5_5	4_4	592.6	-	2.0	1.6	2.3
	5_2	4_1	611.0	-	3.9	4.3	5.6
	5_3	4_2	611.1	-	2.5	2.2	2.8
	5_0	4_{-1}	628.2	-	5.6	5.1	6.0
	5_1	4_0	630.6	-	3.0	2.8	3.2
	5_{-2}	4_{-3}	640.6	-	4.5	4.3	4.8
	5_{-1}	4_{-2}	646.8	-	3.8	3.7	3.9
	5_{-3}	4_{-4}	650.0	-	2.7	2.7	2.8

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	5_{-3}	4_0	80694.8	-	0.8	0.9	0.7
	5_{-5}	4_{-2}	707.8	-	0.6	0.7	0.5
	5_{-2}	4_1	725.6	-	0.5	0.8	-
	5_{-4}	4_{-1}	725.6	-	0.7	0.6	0.6
Q							
	5_4	5_3	646.9	-	0.7	0.5	0.8
	5_3	5_0	665.3	-	0.9	0.7	1.0
	5_2	5_1	666.1	-	1.8	1.5	2.1
	5_1	5_{-2}	679.7	-	1.1	1.0	1.3
	5_0	5_{-1}	689.5	-	3.3	3.0	3.6
	5_{-2}	5_{-3}	716.1	-	8.0	7.9	8.2
	5_{-4}	5_{-5}	734.0	-	23.5	23.8	23.1
	5_{-5}	5_{-4}	736.9	-	12.1	12.4	11.8
	5_{-3}	5_{-2}	743.8	-	4.6	4.9	4.3
	5_{-1}	5_0	767.4	-	2.1	2.4	1.8
	5_{-2}	5_1	780.7	-	3.7	4.3	3.2
	5_{-4}	5_{-1}	787.0	-	1.7	1.9	1.4
	5_1	5_2	792.8	-	1.3	1.5	1.0
	5_0	5_3	794.3	-	2.6	3.1	2.1
	5_3	5_4	812.8	-	0.5	0.7	-
	5_2	5_5	812.8	-	1.0	1.3	0.8

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
				1:0	0:1	1:1	1:-1
R							
	5_0	6_{-3}	80744.2	-	0.8	0.7	0.9
	5_{-2}	6_{-5}	745.5	-	0.8	0.7	0.9
	5_{-3}	6_{-6}	757.0	-	0.6	0.5	0.7
	5_1	6_{-2}	757.5	-	0.7	0.6	0.7
	5_{-1}	6_{-4}	770.6	-	1.4	1.4	1.5
	5_{-3}	6_{-2}	821.7	-	4.5	4.9	4.2
	5_{-5}	6_{-4}	831.6	-	2.9	3.2	2.7
	5_{-1}	6_0	834.8	-	3.9	4.4	3.5
	5_{-4}	6_{-3}	841.7	-	5.8	6.5	5.2
	5_{-2}	6_{-1}	845.3	-	7.5	8.6	6.6
	5_1	6_2	858.2	-	3.5	4.2	3.0
	5_0	6_1	859.6	-	7.1	8.4	6.0
	5_3	6_4	877.9	-	3.0	3.8	2.4
	5_2	6_3	877.9	-	6.1	7.5	4.8
	5_5	6_6	896.6	-	2.4	3.0	1.8
	5_4	6_5	896.6	-	4.7	6.1	3.5
P							
	6_5	5_4	554.6	-	1.0	0.8	1.2
	6_6	5_5	554.6	-	2.0	1.6	2.5
	6_3	5_2	573.0	-	1.4	1.2	1.7
	6_4	5_3	573.0	-	2.9	2.4	3.4

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TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	6_1	5_0	80591.1	-	1.9	1.6	2.1
	6_2	5_1	591.6	-	3.8	3.3	4.2
	6_{-1}	5_{-2}	607.2	-	2.1	2.0	2.3
	6_0	5_{-1}	611.4	-	5.0	4.7	5.3
	6_{-3}	5_{-4}	617.8	-	1.7	1.6	1.8
	6_{-2}	5_{-3}	624.0	-	5.9	5.8	6.0
	6_{-4}	5_{-5}	624.3	-	3.8	3.7	4.0
	6_{-4}	5_{-1}	677.3	-	1.3	1.5	1.1
	6_{-2}	5_1	688.6	-	0.6	0.7	0.5
	6_{-6}	5_{-3}	701.0	-	0.7	0.9	0.6
Q							
	6_4	6_1	638.3	-	0.8	0.7	1.0
	6_2	6_{-1}	656.1	-	1.6	1.3	1.8
	6_1	6_0	658.5	-	0.8	0.7	1.0
	6_0	6_{-3}	666.1	-	1.4	1.2	1.7
	6_{-1}	6_{-2}	685.0	-	1.5	1.4	1.6
	6_{-3}	6_{-4}	712.4	-	4.0	3.9	4.0
	6_{-5}	6_{-6}	728.9	-	10.8	11.0	10.6
	6_{-6}	6_{-5}	730.4	-	21.9	22.4	21.4
	6_{-4}	6_{-3}	732.0	-	9.0	9.4	8.6
	6_{-2}	6_{-1}	753.1	-	3.8	4.2	3.4
	6_{-3}	6_0	776.7	-	1.4	1.7	1.2
	6_0	6_1	781.4	-	2.4	2.8	2.0

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	6_{-1}	6_2	80785.7	-	1.2	1.5	1.0
	6_{-5}	6_{-2}	793.5	-	0.5	0.5	-
	6_2	6_3	803.4	-	1.3	1.7	1.0
	6_1	6_4	803.7	-	0.7	0.8	0.5
	6_4	6_5	822.7	-	0.5	0.6	-
R							
	6_2	7_{-1}	737.1	-	0.5	-	0.5
	6_{-4}	7_{-7}	748.7	-	0.8	0.7	0.9
	6_0	7_{-3}	762.1	-	1.5	1.4	1.6
	6_{-2}	7_{-5}	767.5	-	2.1	2.0	2.2
	6_{-4}	7_{-3}	828.1	-	6.5	7.1	6.0
	6_{-2}	7_{-1}	834.1	-	6.2	6.8	5.5
	6_{-6}	7_{-5}	844.5	-	4.3	4.8	3.8
	6_{-3}	7_{-2}	850.7	-	2.8	3.2	2.5
	6_{-5}	7_{-4}	851.6	-	2.2	2.5	1.9
	6_0	7_1	858.2	-	5.2	6.1	4.4
	6_{-1}	7_0	862.0	-	2.7	3.1	2.2
	6_2	7_3	879.5	-	4.4	5.5	3.5
	6_1	7_2	879.8	-	2.2	2.7	1.8
	6_4	7_5	898.6	-	3.4	4.4	2.6
	6_3	7_4	898.6	-	1.7	2.2	1.3
	6_6	7_7	917.4	-	2.3	3.1	1.7

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TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	6_5	7_6	917.4	-	1.2	1.6	0.8
P							
	7_6	6_5	515.2	-	0.9	0.6	1.1
	7_4	6_3	533.5	-	1.4	1.1	1.7
	7_5	6_4	533.5	-	0.7	0.5	0.8
	7_2	6_1	551.8	-	2.0	1.7	2.3
	7_3	6_2	551.8	-	1.0	0.8	1.2
	7_0	6_{-1}	569.5	-	2.7	2.4	3.0
	7_1	6_0	570.7	-	1.4	1.2	1.5
	7_{-2}	6_{-3}	584.1	-	3.0	2.8	3.3
	7_{-1}	6_{-2}	589.8	-	1.9	1.8	2.0
	7_{-4}	6_{-5}	593.4	-	2.3	2.2	2.5
	7_{-5}	6_{-6}	597.4	-	1.3	1.2	1.3
	7_{-3}	6_{-4}	598.5	-	2.0	2.0	2.1
Q							
	7_2	7_1	628.5	-	0.7	0.6	0.9
	7_1	7_{-2}	644.7	-	0.6	0.5	0.7
	7_0	7_{-1}	650.4	-	1.3	1.1	1.5
	7_{-2}	7_{-3}	680.1	-	2.6	2.4	2.8
	7_{-4}	7_{-5}	707.5	-	7.2	7.1	7.2
	7_{-5}	7_{-4}	720.2	-	4.0	4.1	3.9
	7_{-6}	7_{-7}	722.5	-	18.1	18.5	17.8
	7_{-7}	7_{-6}	723.3	-	9.1	9.3	8.9

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	J''_τ	J'_τ	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	7_{-3}	7_{-2}	80736.7	-	1.6	1.8	1.5
	7_{-1}	7_0	766.8	-	1.0	1.1	0.8
	7_{-4}	7_{-1}	774.1	-	1.8	2.1	1.5
	7_{-2}	7_1	776.2	-	2.0	2.3	1.6
	7_1	7_2	792.0	-	0.6	0.8	0.5
	7_0	7_3	792.9	-	1.2	1.5	1.0
	7_{-6}	7_{-3}	801.9	-	0.5	0.6	-
	7_2	7_5	812.1	-	0.6	0.8	-
R							
	7_{-2}	8_{-5}	739.6	-	0.6	0.5	0.7
	7_{-3}	8_{-6}	760.3	-	0.6	0.6	0.7
	7_{-1}	8_{-4}	763.5	-	0.7	0.7	0.8
	7_{-3}	8_{-2}	833.0	-	2.2	2.5	2.0
	7_{-5}	8_{-4}	835.7	-	2.1	2.4	1.9
	7_{-1}	8_0	855.3	-	1.8	2.1	1.5
	7_{-4}	8_{-3}	856.0	-	4.0	4.6	3.4
	7_{-7}	8_{-6}	856.7	-	1.5	1.7	1.3
	7_{-6}	8_{-5}	861.3	-	3.1	3.6	2.7
	7_{-2}	8_{-1}	863.4	-	3.7	4.4	3.1
	7_1	8_2	879.2	-	1.5	1.9	1.2
	7_0	8_1	880.1	-	3.1	3.7	2.4
	7_3	8_4	898.9	-	1.2	1.5	0.9

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	7_2	8_3	899.0	-	2.3	2.9	1.7
	7_5	8_6	917.9	-	0.8	1.0	0.6
	7_4	8_5	917.9	-	1.6	2.1	1.1
	7_7	8_8	936.9	-	05	0.7	-
	7_6	8_7	936.9	-	1.0	1.4	0.7
P							
	8_6	7_5	492.6	-	0.5	-	0.7
	8_4	7_3	510.9	-	0.9	0.7	1.1
	8_1	7_0	528.9	-	0.7	0.6	0.8
	8_2	7_1	529.1	-	1.3	1.1	1.5
	8_{-1}	7_{-2}	545.9	-	0.9	0.8	1.0
	8_0	7_{-1}	548.4	-	1.9	1.7	2.1
	8_{-3}	7_{-4}	559.2	-	1.0	0.9	1.1
	8_{-2}	7_{-3}	565.4	-	2.6	2.5	2.7
	8_{-5}	7_{-6}	567.6	-	0.8	0.7	0.8
	8_{-6}	7_{-7}	569.8	-	1.6	1.5	1.7
	8_{-4}	7_{-5}	570.5	-	2.5	2.4	2.6
	8_{-4}	7_{-1}	637.1	-	0.5	0.6	-
	8_{-6}	7_{-3}	649.2	-	0.5	0.6	-
Q							
	8_2	8_{-1}	616.4	-	0.5	-	0.7
	8_0	8_{-3}	630.2	-	0.7	0.5	0.8
	8_{-1}	8_{-2}	642.3	-	0.5	-	0.5
	8_{-3}	8_{-4}	674.7	-	1.0	1.0	1.1

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	8_{-5}	8_{-6}	80701.0	-	3.0	3.0	3.0
	8_{-6}	8_{-5}	708.6	-	6.4	6.5	6.2
	8_{-7}	8_{-8}	715.2	-	7.0	7.2	6.9
	8_{-8}	8_{-7}	715.5	-	14.1	14.4	13.8
	8_{-4}	8_{-3}	719.0	-	2.6	2.8	2.4
	8_{-2}	8_{-1}	748.7	-	1.4	1.6	1.2
	8_{-3}	8_{0}	766.5	-	0.7	0.8	0.6
	8_{-5}	8_{-2}	773.7	-	0.5	0.6	-
	8_{0}	8_{1}	778.0	-	0.9	1.2	0.7
	8_{-1}	8_{2}	780.5	-	0.5	0.6	-
	8_{2}	8_{3}	799.6	-	0.5	0.7	-
R	8_{0}	9_{-3}	743.8	-	0.5	-	0.5
	8_{-4}	9_{-7}	749.8	-	0.7	0.6	0.8
	8_{-2}	9_{-5}	760.9	-	1.1	1.0	1.3
	8_{-4}	9_{-3}	832.6	-	2.9	3.2	2.6
	8_{-6}	9_{-5}	844.6	-	2.6	2.9	2.3
	8_{-2}	9_{-1}	849.8	-	2.3	2.6	2.0
	8_{-5}	9_{-4}	861.3	-	1.3	1.5	1.1
	8_{-3}	9_{-2}	864.3	-	1.2	1.4	1.0
	8_{-8}	9_{-7}	867.9	-	2.0	2.3	1.7
	8_{-7}	9_{-6}	870.6	-	1.0	1.2	0.9
	8_{0}	9_{1}	876.5	-	1.9	2.3	1.5

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	8_{-1}	9_0	80378.8	-	1.0	1.2	0.8
	8_2	9_3	897.5	-	1.5	1.9	1.1
	8_1	9_2	897.7	-	0.7	0.9	0.6
	8_4	9_5	916.9	-	1.0	1.3	0.7
	8_3	9_4	916.9	-	0.5	0.7	-
	8_6	9_7	936.0	-	0.6	0.8	-
P							
	9_2	8_1	486.6	-	0.5	-	0.7
	9_0	8_{-1}	504.4	-	0.8	0.7	0.9
	9_{-2}	8_{-3}	520.5	-	1.1	1.0	1.2
	9_{-1}	8_{-2}	524.3	-	0.6	0.6	0.7
	9_{-4}	8_{-5}	532.4	-	1.2	1.1	1.3
	9_{-3}	8_{-4}	538.1	-	0.8	0.8	0.8
	9_{-5}	8_{-6}	540.5	-	0.7	0.7	0.8
	9_{-6}	8_{-7}	540.5	-	0.9	0.9	1.0
	9_{-7}	8_{-8}	541.7	-	0.5	-	0.5
Q							
	9_{-2}	9_{-3}	634.1	-	0.6	0.6	0.7
	9_{-4}	9_{-5}	668.4	-	1.6	1.5	1.6
	9_{-6}	9_{-7}	692.9	-	4.5	4.5	4.4
	9_{-7}	9_{-6}	697.2	-	2.3	2.4	2.3
	9_{-5}	9_{-4}	700.8	-	1.0	1.0	0.9
	9_{-8}	9_{-9}	706.8	-	10.2	10.4	10.0
	9_{-9}	9_{-8}	707.0	-	5.1	5.2	5.0

APPX. V

TABLE V.3 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	9_{-3}	9_{-2}	80727.7	-	0.5	0.5	-
	9_{-4}	9_{-1}	757.4	-	0.8	1.0	0.7
	9_{-2}	9_{1}	766.8	-	0.7	0.8	0.5
	9_{-6}	9_{-3}	775.7	-	0.5	0.6	-
R							
	9_{-5}	10_{-4}	833.6	-	0.9	1.0	0.8
	9_{-3}	10_{-2}	842.7	-	0.7	0.8	0.6
	9_{-7}	10_{-6}	854.1	-	0.8	0.9	0.7
	9_{-4}	10_{-3}	866.6	-	1.6	1.9	1.4
	9_{-6}	10_{-5}	864.7	-	1.5	1.8	1.2
	9_{-1}	10_{0}	870.9	-	0.6	0.7	0.5
	9_{-2}	10_{-1}	876.3	-	1.2	1.5	1.0
	9_{-9}	10_{-8}	877.9	-	0.7	0.8	0.6
	9_{-8}	10_{-7}	879.4	-	1.3	1.6	1.1
	9_{0}	10_{1}	894.7	-	0.9	1.1	0.7
	9_{2}	10_{3}	914.2	-	0.6	0.8	-
P							
	10_{0}	9_{-1}	479.2	-	0.5	-	0.6
	10_{-2}	9_{-3}	497.9	-	0.8	0.7	0.8
	10_{-4}	9_{-5}	508.2	-	0.9	0.9	1.0
	10_{-6}	9_{-7}	509.3	-	0.8	0.7	0.8
	10_{-8}	9_{-9}	513.0	-	0.6	0.5	0.6

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TABLE V.3 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
				1:0	0:1	1:1	1:-1
Q							
	10_{-5}	10_{-6}	80661.0	-	0.6	0.5	0.6
	10_{-6}	10_{-5}	683.0	-	1.4	1.4	1.3
	10_{-7}	10_{-8}	683.3	-	1.5	1.6	1.5
	10_{-8}	10_{-7}	685.6	-	3.2	3.2	3.1
	10_{-9}	10_{-10}	697.5	-	3.5	3.5	3.4
	10_{-10}	10_{-9}	697.6	-	6.9	7.1	6.8
	10_{-4}	10_{-3}	704.5	-	0.6	0.6	0.5
R							
	10_{-4}	11_{-3}	835.1	-	0.8	0.9	0.7
	10_{-6}	11_{-5}	836.4	-	0.9	1.0	0.8
	10_{-2}	11_{-1}	862.2	-	0.6	0.7	0.5
	10_{-8}	11_{-7}	863.2	-	0.9	1.1	0.8
	10_{-7}	11_{-6}	871.9	-	0.5	0.6	-
	10_{-10}	11_{-9}	886.7	-	0.8	1.0	0.7
	10_{0}	11_{1}	888.8	-	0.5	0.6	-

APPX. V TABLE V.4

$\tilde{D}^1A_1$ Transitions in D_2O Calculated for Various Ratio $\langle\mu_z\rangle : \langle\mu_x\rangle$

(Electronic interaction)

IDENTIFICATION			FREQUENCY	*RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
R	0_0	1_0	82095.3	6.7	-	6.4	7.0
P	1_0	0_0	2054.6	6.0	-	6.0	6.0
Q	1_1	1_{-1}	2063.0	4.5	-	4.5	4.5
	1_{-1}	1_1	2085.2	4.7	-	4.5	4.9
R	1_0	2_{-2}	2086.6	3.9	-	3.8	3.9
	1_{-1}	2_{-1}	2102.7	4.7	-	4.5	4.9
	1_1	2_1	2127.2	4.5	-	4.1	4.9
	1_0	2_2	2129.9	8.2	-	7.4	9.0
P	2_2	1_0	2021.2	6.0	-	6.3	5.7
	2_1	1_1	2023.6	3.5	-	3.6	3.3
	2_{-1}	1_{-1}	2043.6	4.1	-	4.0	4.1
	2_{-2}	1_0	2059.4	3.9	-	3.8	4.0
Q	2_1	2_{-1}	2041.2	1.9	-	2.0	1.8
	2_2	2_0	2046.6	5.4	-	5.6	5.3
	2_0	2_{-2}	2057.5	11.8	-	11.9	11.8
	2_{-2}	2_0	2084.8	12.1	-	11.5	12.7
	2_0	2_2	2100.8	5.6	-	5.1	6.1
	2_{-1}	2_1	2107.8	2.3	-	2.1	2.5

*Values of $[I]^{J''}_{J'}$ x10 less than 0.5 are not included for $\langle\mu_z\rangle : \langle\mu_x\rangle$ = 1:0 and the corresponding cases of 1:1, 0:1 and 1:-1 in this table.

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TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
R							
	2_2	3_{-2}	82069.8	0.5	-	0.5	-
	2_1	3_{-1}	2082.1	0.5	-	0.6	0.5
	2_{-1}	3_{-3}	2095.9	3.9	-	3.9	4.0
	2_{-2}	3_{-2}	2108.0	11.9	-	11.3	12.4
	2_0	3_0	2132.7	8.7	-	7.9	9.5
	2_{-1}	3_1	2141.3	3.3	-	2.9	3.6
	2_2	3_2	2161.5	11.2	-	9.7	12.8
	2_1	3_3	2162.0	5.6	-	4.9	6.4
P							
	3_3	2_1	1992.9	3.7	-	4.1	3.3
	3_2	2_2	1993.2	7.5	-	8.2	6.8
	3_1	2_{-1}	2002.6	2.0	-	2.2	1.9
	3_0	2_0	2010.7	6.5	-	6.8	6.2
	3_{-2}	2_{-2}	2032.3	9.7	-	9.7	9.7
	3_{-3}	2_{-1}	2044.3	3.8	-	3.7	3.9
	3_{-1}	2_1	2060.9	0.6	-	0.5	0.6
	3_{-2}	2_2	2075.6	0.7	-	0.6	0.7
Q							
	3_2	3_0	2025.2	3.1	-	3.3	2.9
	3_3	3_1	2026.4	1.6	-	1.7	1.5
	3_0	3_{-2}	2033.9	5.3	-	5.6	5.0
	3_1	3_{-1}	2043.5	4.7	-	4.8	4.6

APPX. V

TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	3_{-1}	3_{-3}	82049.0	5.8	-	5.9	5.8
	3_{-3}	3_{-1}	2085.2	5.7	-	5.3	6.0
	3_{-1}	3_{1}	2094.4	4.5	-	4.1	4.8
	3_{-2}	3_{0}	2107.5	6.1	-	5.5	6.8
	3_{1}	3_{3}	2123.5	1.9	-	1.6	2.1
	3_{0}	3_{2}	2125.7	3.8	-	3.3	4.2
R							
	3_{0}	4_{-2}	2092.0	2.3	-	2.3	2.3
	3_{-2}	4_{-4}	2103.9	11.2	-	10.9	11.5
	3_{-3}	4_{-3}	2111.9	6.8	-	6.6	7.1
	3_{-1}	4_{-1}	2135.8	4.2	-	3.8	4.6
	3_{-2}	4_{0}	2154.0	4.6	-	4.1	5.2
	3_{1}	4_{1}	2166.8	4.6	-	4.0	5.3
	3_{0}	4_{2}	2169.2	9.3	-	8.0	10.7
	3_{3}	4_{3}	2196.5	5.3	-	4.3	6.3
	3_{2}	4_{4}	2196.6	10.5	-	8.7	12.6
P							
	4_{4}	3_{2}	1965.0	6.0	-	6.9	5.2
	4_{3}	3_{3}	1965.0	3.0	-	3.4	2.6
	4_{2}	3_{0}	1975.5	5.5	-	6.1	5.0
	4_{1}	3_{1}	1977.2	2.9	-	3.2	2.6
	4_{0}	3_{-2}	1979.7	2.2	-	2.4	2.0
	4_{-1}	3_{-1}	1997.6	2.9	-	3.1	2.8

APPX. V

TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	4_{-3}	3_{-3}	2020.6	5.3	-	5.3	5.3
	4_{-4}	3_{-2}	2028.8	10.1	-	9.9	10.3
	4_{-2}	3_{0}	2040.9	2.4	-	2.3	2.5
	4_{-3}	3_{1}	2066.0	0.5	-	-	0.5
	4_{0}	3_{2}	2071.4	0.5	-	-	0.5
Q							
	4_{3}	4_{1}	2008.4	0.9	-	1.0	0.8
	4_{4}	4_{2}	2008.5	1.8	-	2.1	1.6
	4_{1}	4_{-1}	2018.6	2.2	-	2.4	2.1
	4_{2}	4_{0}	2022.0	5.0	-	5.4	4.7
	4_{-1}	4_{-3}	2024.3	2.7	-	2.8	2.5
	4_{-2}	4_{-4}	2037.3	9.4	-	9.7	9.2
	4_{0}	4_{-2}	2037.8	11.3	-	11.6	11.1
	4_{-4}	4_{-2}	2086.9	8.7	-	8.1	9.4
	4_{-2}	4_{0}	2087.4	10.2	-	9.4	11.1
	4_{-3}	4_{-1}	2107.4	3.1	-	2.7	3.4
	4_{0}	4_{2}	2115.0	5.2	-	4.6	5.9
	4_{-1}	4_{1}	2121.0	2.6	-	2.3	3.0
	4_{2}	4_{4}	2146.9	2.4	-	2.0	2.8
	4_{1}	4_{3}	2147.3	1.2	-	1.0	1.4
R							
	4_{2}	5_{-2}	2071.3	0.5	-	0.6	0.5
	4_{-1}	5_{-3}	2101.0	1.7	-	1.7	1.7

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TABLE V.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch $J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	4_{-3} 5_{-5}	82110.4	6.5	-	6.4	6.7
	4_{-4} 5_{-4}	2115.1	14.4	-	13.9	15.0
	4_{-2} 5_{-2}	2136.7	7.8	-	7.1	8.5
	4_{-3} 5_{-1}	2168.6	1.4	-	1.2	1.6
	4_{0} 5_{0}	2169.2	7.2	-	6.2	8.3
	4_{-1} 5_{1}	2176.0	3.6	-	3.1	4.1
	4_{2} 5_{2}	2201.2	8.2	-	6.7	9.8
	4_{1} 5_{3}	2201.6	4.1	-	3.4	4.9
	4_{-4} 5_{0}	2218.4	0.5	-	-	0.6
	4_{4} 5_{4}	2232.6	7.7	-	6.1	9.6
	4_{3} 5_{5}	2232.6	3.9	-	3.0	4.8
P						
	5_{5} 4_{3}	1938.2	1.9	-	2.3	1.6
	5_{4} 4_{4}	1938.2	3.8	-	4.5	3.1
	5_{3} 4_{1}	1946.7	2.2	-	2.5	1.9
	5_{2} 4_{2}	1946.9	4.4	-	5.0	3.7
	5_{-1} 4_{-3}	1952.2	0.5	-	0.6	0.5
	5_{1} 4_{-1}	1955.5	1.8	-	2.0	1.6
	5_{0} 4_{0}	1960.7	4.3	-	4.8	3.9
	5_{-2} 4_{-2}	1984.3	5.2	-	5.4	5.0
	5_{-4} 4_{-4}	2008.1	10.7	-	10.7	10.8
	5_{-5} 4_{-3}	2013.2	5.4	-	5.3	5.5

APPX. V

TABLE V.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	5_{-3}	4_{-1}	82019.6	1.7	-	1.6	1.7
	5_{-4}	4_0	2058.2	0.8	-	0.7	0.9
	5_{-2}	4_2	2061.6	0.8	-	0.8	0.9
Q							
	5_4	5_2	1992.5	0.9	-	1.1	0.8
	5_5	5_3	1992.5	0.5	-	0.5	-
	5_2	5_0	2001.1	2.6	-	2.9	2.3
	5_3	5_1	2001.7	1.3	-	1.5	1.2
	5_0	5_{-2}	2010.0	4.7	-	5.1	4.3
	5_{-2}	5_{-4}	2012.5	4.6	-	4.9	4.2
	5_1	5_{-1}	2016.6	3.0	-	3.1	2.8
	5_{-3}	5_{-5}	2022.6	3.4	-	3.5	3.2
	5_{-1}	5_{-3}	2028.9	5.4	-	5.5	5.3
	5_{-3}	5_{-1}	2080.8	4.7	-	4.3	5.1
	5_{-5}	5_{-3}	2089.9	3.1	-	2.8	3.4
	5_{-1}	5_1	2103.9	2.7	-	2.4	3.0
	5_{-4}	5_{-2}	2107.5	5.3	-	4.6	5.9
	5_{-2}	5_0	2115.8	5.3	-	4.6	6.0
	5_1	5_3	2138.4	1.6	-	1.3	1.9
	5_0	5_2	2139.9	3.2	-	2.7	3.8
	5_3	5_5	2170.9	0.7	-	0.5	0.8
	5_2	5_4	2170.9	1.3	-	1.0	1.6

APPX. V

TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
R							
	5_0	6_{-2}	82087.8	1.0	-	1.0	1.0
	5_{-2}	6_{-4}	2109.0	4.1	-	4.0	4.2
	5_{-4}	6_{-6}	2115.3	13.2	-	12.8	13.6
	5_{-5}	6_{-5}	2117.9	6.9	-	6.7	7.2
	5_{-3}	6_{-3}	2135.9	3.5	-	3.3	3.8
	5_{-1}	6_{-1}	2168.6	2.7	-	2.3	3.1
	5_{-4}	6_{-2}	2185.2	1.7	-	1.4	1.9
	5_{-2}	6_0	2183.0	5.1	-	4.3	5.9
	5_1	6_1	2203.7	3.0	-	2.4	3.6
	5_0	6_2	2205.3	6.1	-	4.9	7.3
	5_3	6_3	2236.0	2.8	-	2.2	3.5
	5_2	6_4	2236.0	5.7	-	4.4	7.1
	5_5	6_5	2269.9	2.3	-	1.7	3.0
	5_4	6_6	2269.9	4.6	-	3.4	6.0
P							
	6_4	5_2	1918.6	2.6	-	3.1	2.1
	6_3	5_3	1918.6	1.3	-	1.6	1.1
	6_6	5_4	1912.7	2.0	-	2.4	1.5
	6_5	5_5	1912.7	1.0	-	1.2	0.8
	6_2	5_0	1926.6	2.9	-	3.3	2.5
	6_1	5_1	1927.5	1.5	-	1.7	1.3
	6_0	5_{-2}	1931.9	2.1	-	2.3	1.8
	6_{-1}	5_{-1}	1944.1	1.5	-	1.7	1.4

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TABLE V.4

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
				1:0	0:1	1:1	1:-1
	6_{-3}	5_{-3}	81970.8	2.2	-	2.3	2.2
	6_{-5}	5_{-5}	1994.4	5.0	-	4.9	5.0
	6_{-6}	5_{-4}	1997.4	10.2	-	10.0	10.3
	6_{-4}	5_{-2}	1997.8	3.8	-	3.8	3.9
	6_{-2}	5_{0}	2023.6	1.1	-	1.0	1.2
	6_{-3}	5_{1}	2045.7	0.5	-	-	0.5
Q							
	6_{3}	6_{1}	1983.9	0.6	-	0.7	0.5
	6_{4}	6_{2}	1984.0	1.2	-	1.4	1.0
	6_{1}	6_{-1}	1992.2	1.3	-	1.5	1.2
	6_{2}	6_{0}	1993.8	2.8	-	3.0	2.5
	6_{-3}	6_{-5}	1998.7	1.8	-	1.9	1.6
	6_{-1}	6_{-3}	1999.2	2.1	-	2.2	1.9
	6_{-4}	6_{-6}	2005.7	4.4	-	4.7	4.2
	6_{0}	6_{-2}	2009.6	6.0	-	6.2	5.7
	6_{-2}	6_{-4}	2016.8	8.5	-	8.7	8.2
	6_{-4}	6_{-2}	2075.5	7.0	-	6.3	7.6
	6_{-2}	6_{0}	2090.8	4.8	-	4.3	5.4
	6_{-6}	6_{-4}	2093.8	4.2	-	3.7	4.7
	6_{-5}	6_{-3}	2107.7	2.0	-	1.8	2.3
	6_{-3}	6_{-1}	2110.4	2.2	-	1.9	2.6
	6_{0}	6_{2}	2127.1	3.0	-	2.5	3.5

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TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	6_{-1}	6_1	82131.2	1.5	-	1.3	1.8
	6_2	6_4	2161.6	1.7	-	1.3	2.0
	6_1	6_3	2161.8	0.8	-	0.7	1.0
	6_4	6_6	2196.0	0.6	-	0.5	0.8
R							
	6_{-1}	7_{-3}	2095.3	0.6	-	0.6	0.5
	6_{-3}	7_{-5}	2115.5	2.2	-	2.1	2.2
	6_{-5}	7_{-7}	2118.9	6.0	-	5.8	6.2
	6_{-6}	7_{-6}	2120.1	12.2	-	11.8	12.7
	6_{-4}	7_{-4}	2134.1	6.1	-	5.7	6.5
	6_{-2}	7_{-2}	2165.2	3.9	-	3.4	4.4
	6_{-3}	7_{-1}	2191.0	1.6	-	1.3	1.9
	6_0	7_0	2203.5	4.0	-	3.3	4.8
	6_{-5}	7_{-3}	2203.8	0.5	-	-	0.5
	6_{-1}	7_1	2207.9	2.1	-	1.7	2.5
	6_{-6}	7_{-2}	2242.2	0.5	-	-	0.6
	6_2	7_2	2237.7	3.9	-	3.0	4.9
	6_1	7_3	2237.9	2.0	-	1.5	2.5
	6_4	7_4	2271.9	3.2	-	2.3	4.2
	6_3	7_5	2271.9	1.6	-	1.2	2.1
	6_5	7_7	2308.4	1.2	-	0.8	1.5
	6_6	7_6	2308.4	2.3	-	1.6	3.1

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TABLE V.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch J''_τ	J'_τ	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
P						
7_6	6_6	81888.5	0.8	-	1.1	0.6
7_5	6_3	1891.6	0.6	-	0.8	0.5
7_4	6_4	1891.6	1.3	-	1.6	1.0
7_3	6_1	1897.3	0.8	-	1.0	0.7
7_2	6_2	1897.4	1.7	-	2.0	1.4
7_{-1}	6_{-3}	1904.0	0.5	-	0.6	-
7_1	6_{-1}	1904.4	0.9	-	1.0	0.7
7_0	6_0	1907.2	1.9	-	2.2	1.6
7_{-2}	6_{-2}	1927.6	2.1	-	2.3	1.9
7_{-4}	6_{-4}	1956.9	3.7	-	3.8	3.6
7_{-5}	6_{-3}	1976.3	1.8	-	1.8	1.9
7_{-6}	6_{-6}	1979.5	8.5	-	8.4	8.6
7_{-7}	6_{-5}	1981.1	4.3	-	4.3	4.4
7_{-3}	6_{-1}	1996.5	0.6	-	0.6	0.6
7_{-4}	6_0	2030.8	0.8	-	0.7	0.8
7_{-2}	6_2	2045.2	0.5	-	-	0.5
Q						
7_4	7_2	1967.7	0.5	-	0.6	-
7_2	7_{-6}	1973.8	1.2	-	1.4	1.0
7_3	7_1	1974.0	0.6	-	0.7	0.5
7_0	7_{-2}	1981.5	2.3	-	2.5	2.0
7_{-4}	7_{-6}	1983.2	2.5	-	2.7	2.2

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TABLE V.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch $J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	7_1 7_{-1}	81984.9	1.3	-	1.4	1.1
	7_{-2} 7_2	1986.2	3.2	-	3.4	2.9
	7_{-5} 7_{-7}	1987.4	1.4	-	1.5	1.3
	7_{-1} 7_{-3}	2000.1	2.6	-	2.7	2.5
	7_{-3} 7_{-5}	2001.5	2.9	-	3.0	2.7
	7_{-5} 7_{-3}	2072.3	2.2	-	2.0	2.5
	7_{-3} 7_{-1}	2077.0	1.9	-	1.7	2.2
	7_{-7} 7_{-5}	2097.9	1.4	-	1.2	1.6
	7_{-4} 7_{-2}	2105.2	3.4	-	2.9	3.9
	7_{-6} 7_{-4}	2108.0	2.9	-	2.5	3.4
	7_{-1} 7_1	2112.6	1.2	-	1.0	1.4
	7_{-2} 7_{-6}	2121.5	2.5	-	2.1	3.0
	7_1 7_3	2150.1	0.7	-	0.6	0.9
	7_0 7_2	2151.0	1.5	-	1.2	1.9
	7_2 7_6	2185.4	0.7	-	0.6	0.9
R						
	7_{-2} 8_{-4}	2102.2	1.1	-	1.1	1.1
	7_{-4} 8_{-6}	2120.3	4.0	-	3.9	4.2
	7_{-6} 8_{-8}	2121.2	9.9	-	9.6	10.2
	7_{-7} 8_{-7}	2121.8	5.0	-	4.8	5.2
	7_{-5} 8_{-5}	2132.1	2.5	-	2.3	2.7
	7_{-3} 8_{-3}	2159.6	1.4	-	1.2	1.6

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TABLE V.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]_{J'}^{J''}$ x 10 FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch $J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	7_{-1} 8_{-1}	82200.0	1.3	-	1.0	1.5
	7_{-4} 8_{-2}	2200.8	1.8	-	1.5	2.2
	7_{-2} 8_{0}	2209.9	2.7	-	2.2	3.3
	7_{-6} 8_{-4}	2223.9	0.5	-	-	0.6
	7_{1} 8_{1}	2237.3	1.3	-	1.0	1.6
	7_{0} 8_{2}	2238.2	2.6	-	2.0	3.2
	7_{3} 8_{3}	2272.2	1.0	-	0.8	1.4
	7_{2} 8_{4}	2272.3	2.1	-	1.5	2.7
	7_{5} 8_{5}	2308.9	0.7	-	0.5	1.0
	7_{4} 8_{6}	2308.9	1.5	-	1.1	2.0
	7_{7} 8_{7}	2348.0	0.5	-	-	0.7
	7_{6} 8_{8}	2348.0	1.0	-	0.6	1.3
P						
	8_{6} 7_{4}	1865.9	0.5	-	0.7	-
	8_{4} 7_{2}	1869.0	0.8	-	1.0	0.6
	8_{2} 7_{0}	1874.4	1.0	-	1.2	0.8
	8_{1} 7_{1}	1874.8	0.5	-	0.6	-
	8_{0} 7_{-2}	1879.4	1.0	-	1.1	0.8
	8_{-1} 7_{-1}	1886.2	0.6	-	0.7	0.5
	8_{-3} 7_{-3}	1911.3	0.7	-	0.8	0.7
	8_{-5} 7_{-5}	1942.2	1.4	-	1.5	1.4

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TABLE V.4 (Continued)

IDENTIFICATION			FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	$J''_{\tau''}$	$J'_{\tau'}$	ν (cm^{-1})	1:0	0:1	1:1	1:-1
	8_{-6}	7_{-4}	81955.3	3.1	-	3.1	3.1
	8_{-7}	7_{-7}	1963.4	3.3	-	3.3	3.4
	8_{-8}	7_{-6}	1964.3	6.7	-	6.7	6.8
	8_{-4}	7_{-2}	1968.2	1.1	-	1.0	1.1
Q							
	8_{4}	8_{2}	1956.2	0.5	-	0.5	-
	8_{1}	8_{-1}	1962.1	0.5	-	0.6	-
	8_{2}	8_{0}	1962.8	1.0	-	1.1	0.9
	8_{-5}	8_{-7}	1966.1	0.8	-	0.9	0.7
	8_{-6}	8_{-8}	1968.4	1.7	-	1.9	1.5
	8_{-1}	8_{-3}	1968.8	0.9	-	1.0	0.8
	8_{-3}	8_{-5}	1971.1	1.1	-	1.2	1.0
	8_{0}	8_{-2}	1975.0	2.1	-	2.2	1.9
	8_{-4}	8_{-6}	1983.3	3.4	-	3.6	3.2
	8_{-2}	8_{-4}	1987.4	3.8	-	4.0	3.7
	8_{-4}	8_{-2}	2063.8	2.7	-	2.4	3.0
	8_{-6}	8_{-4}	2071.2	2.6	-	2.2	2.9
	8_{-2}	8_{0}	2095.1	1.6	-	1.4	1.9
	8_{-5}	8_{-3}	2100.3	1.1	-	1.0	1.4
	8_{-8}	8_{-6}	2101.4	1.9	-	1.6	2.2
	8_{-7}	8_{-5}	2108.1	1.0	-	0.8	1.2
	8_{-3}	8_{-1}	2111.2	0.9	-	0.7	1.1

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TABLE V.4 (Continued)

IDENTIFICATION Branch	$J''_{\tau''}$	$J'_{\tau'}$	FREQUENCY ν (cm^{-1})	RELATIVE INTENSITY $[I]^{J''}_{J'}$ x 10 FOR $\langle\mu_z\rangle : \langle\mu_x\rangle$			
				1:0	0:1	1:1	1:-1
	8_0	8_2	82136.2	1.1	-	0.9	1.4
	8_{-1}	8_1	2138.6	0.6	-	0.5	0.7
	8_2	8_4	2172.9	0.6	-	0.5	0.8
R							
	8_{-3}	9_{-5}	2108.2	0.5	-	0.5	0.5
	8_{-7}	9_{-9}	2122.4	3.8	-	3.7	3.9
	8_{-8}	9_{-8}	2122.7	7.6	-	7.4	0.8
	8_{-5}	9_{-7}	2123.2	1.7	-	1.6	1.7
	8_{-6}	9_{-6}	2130.2	3.8	-	3.5	4.0
	8_{-4}	9_{-4}	2152.6	1.9	-	1.7	2.2
	8_{-2}	9_{-2}	2193.1	1.5	-	1.2	1.8
	8_{-3}	9_{-1}	2211.9	0.8	-	0.7	1.0
	8_{-5}	9_{-3}	2212.8	0.5	-	-	0.6
	8_0	9_0	2234.5	1.5	-	1.2	1.9
	8_{-1}	9_1	2237.1	0.8	-	0.6	1.0
	8_2	9_2	2270.9	1.3	-	0.9	1.7
	8_1	9_3	2271.0	0.6	-	0.5	0.8
	8_4	9_4	2307.9	0.9	-	0.6	1.2
	8_3	9_5	2307.9	0.5	-	-	0.6
	8_6	9_6	2347.1	0.6	-	-	0.8
P	9_0	8_0	81850.8	0.6	-	0.7	0.5

APPX. V

TABLE V.4 (Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch $J''_{\tau''}$	$J'_{\tau'}$	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	9_{-2} 8_{-2}	81865.3	0.7	-	0.8	0.6
	9_{-4} 8_{-4}	1895.0	1.0	-	1.0	0.9
	9_{-6} 8_{-6}	1926.4	2.2	-	2.2	2.1
	9_{-7} 8_{-5}	1934.7	1.1	-	1.2	1.1
	9_{-8} 8_{-8}	1946.2	4.9	-	4.8	4.9
	9_{-9} 8_{-7}	1946.6	2.5	-	2.4	2.5
Q						
	9_{-6} 9_{-8}	1947.7	1.0	-	1.1	0.9
	9_{0} 9_{-2}	1948.8	0.7	-	0.8	0.6
	9_{-7} 9_{-9}	1948.9	0.5	-	0.6	-
	9_{-4} 9_{-6}	1954.0	1.4	-	1.5	1.2
	9_{-2} 9_{-4}	1954.1	1.2	-	1.3	1.0
	9_{-5} 9_{-7}	1962.7	0.9	-	1.0	0.9
	9_{-1} 9_{-3}	1963.4	0.8	-	0.8	0.7
	9_{-3} 9_{-5}	1971.6	1.2	-	1.3	1.2
	9_{-5} 9_{-3}	2052.3	0.8	-	0.7	0.9
	9_{-7} 9_{-5}	2071.7	0.7	-	0.6	0.8
	9_{-3} 9_{-1}	2075.3	0.5	-	-	0.6
	9_{-6} 9_{-4}	2095.7	1.4	-	1.2	1.7
	9_{-4} 9_{-2}	2100.7	1.2	-	1.0	1.4
	9_{-9} 9_{-7}	2103.8	0.6	-	0.5	0.7

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TABLE V.4(Continued)

IDENTIFICATION		FREQUENCY	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
Branch	J''_τ J'_τ	$\nu(cm^{-1})$	1:0	0:1	1:1	1:-1
	9_{-8} 9_{-6}	82108.0	1.2	-	1.0	1.5
	9_{-2} 9_0	2124.8	0.8	-	0.6	1.0
	9_0 9_2	2158.9	0.5	-	-	0.6
R						
	9_{-4} 10_{-6}	2112.8	0.8	-	0.8	0.8
	9_{-8} 10_{-10}	2122.5	5.5	-	5.3	5.7
	9_{-9} 10_{-9}	2122.7	2.7	-	2.6	2.8
	9_{-6} 10_{-8}	2124.4	2.5	-	2.4	2.6
	9_{-7} 10_{-7}	2128.3	1.3	-	1.3	1.4
	9_{-5} 10_{-5}	2145.0	0.7	-	0.6	0.7
	9_{-4} 10_{-2}	2214.8	0.9	-	0.7	1.1
	9_{-6} 10_{-4}	2227.3	0.5	-	-	0.6
	9_{-2} 10_0	2234.8	0.9	-	0.7	1.1
	9_0 10_2	2268.1	0.7	-	0.5	1.0
	9_2 10_4	2305.2	0.5	-	-	0.7
P						
	10_{-7} 9_{-7}	1909.3	0.7	-	0.8	0.7
	10_{-6} 9_{-4}	1912.1	0.7	-	0.7	0.7
	10_{-8} 9_{-6}	1914.2	1.6	-	1.6	1.6
	10_{-9} 9_{-9}	1928.0	1.7	-	1.7	1.7
	10_{-10} 9_{-8}	1928.2	3.4	-	3.3	3.4

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TABLE V.4(Continued)

IDENTIFICATION Branch J''_τ J'_τ	FREQUENCY $\nu(cm^{-1})$	RELATIVE INTENSITY $[I]^{J''}_{J'} \times 10$ FOR $\langle \mu_z \rangle : \langle \mu_x \rangle$			
		1:0	0:1	1:1	1:-1
Q					
$10_{-8}10_{-10}$	81928.7	0.6	-	0.7	0.5
$10_{0}10_{-2}$	1936.6	0.5	-	0.6	0.5
$10_{-6}10_{-8}$	1940.7	1.0	-	1.1	0.9
$10_{-2}10_{-4}$	1949.5	1.0	-	1.1	1.0
$10_{-4}10_{-6}$	1952.6	1.4	-	1.4	1.3
$10_{-6}10_{-4}$	2043.7	0.9	-	0.7	1.0
$10_{-4}10_{-2}$	2054.5	0.6	-	0.5	0.7
$10_{-8}10_{-6}$	2073.0	0.8	-	0.7	0.9
$10_{-10}10_{-8}$	2104.9	0.7	-	0.6	0.9
R					
$10_{-9}11_{-11}$	2121.7	1.8	-	1.8	1.9
$10_{-10}11_{-10}$	2121.8	3.7	-	3.6	3.8
$10_{-7}11_{-9}$	2124.0	0.9	-	0.8	0.9
$10_{-8}11_{-8}$	2126.1	1.8	-	1.7	1.9
$10_{-6}11_{-6}$	2137.5	0.8	-	0.8	0.9
$10_{4}11_{-4}$	2171.2	0.5	-	-	0.6

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